TECHNOLOGY SURVEY

Technology Utilization Division

HANDLING
HAZARDOUS
MATERIALS

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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Foreword

The Administrator of the National Aeronautics and Space Administration has established a technology utilization program for "the rapid dissemination of information . . . on technological developments . . . which appear to be useful for general industrial application." From a variety of sources, including NASA Research Centers and NASA contractors, space-related technology is collected and screened; and that which has potential industrial use is made generally available. Information from the nation's space program is thus made available to American industry, including the latest developments in materials, processes, products, techniques, management systems, and analytical and design procedures.

This publication is part of a series intended to provide such technical information. It deals with highly reactive materials that have been studied in the search for fuels and oxidizers for space work: Liquid hydrogen, pentaborane, fluorine, chlorine trifluoride, ozone, nitrogen tetroxide, and hydrazine and its derivatives. It describes both the hazards that have restricted the use of these materials and the procedures by which they have been handled and stored safely. References are given to work done by NASA and other investigators. Since such work is continuing, it is likely that further knowledge will be generated—some of which may supersede or amplify material presented here.

THE DIRECTOR, *Technology Utilization Division*
National Aeronautics and Space Administration

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Introduction

The NASA-generated program of space engineering is rapidly creating new processes and manufacturing techniques, new methods of testing, new materials, and advanced designs for power sources, propulsion systems, and electronic components. Many of these innovations presently apply only to space vehicles or pertinent support activities. But some such developments may enable industry to cut costs and improve reliability in areas which have little or no relation to the space program. Intensive efforts are under way to identify such new products, processes, and other useful innovations as they appear in NASA research centers or at contractors' plants, and to make them known and available for general use.

During the last ten years much research has been carried out in the field of high-energy fuels and oxidizers to provide for the military's guided missile and aeronautical programs. This research has carried over into the development of NASA launch-vehicles and propulsion systems.

Before the inception of NASA, the military services developed such pioneering boosters as Jupiter-C, Vanguard, and the Redstone. Considerable research went into the development of propellants and propulsion for them. The liquid fuels commonly in use then, and even now, are RP-1 (a petroleum fraction such as kerosene), alcohols (chiefly ethyl alcohol), and ammonia. As oxidizers, liquid oxygen, the nitric acids, hydrogen peroxide, and nitrogen tetroxide are used.

As interplanetary space missions have become feasible, weight-scrimping high-impulse propellants have been sought, and NASA has brought some of these propellants to an advanced state of development. Among these are hydrazine and certain hydrazine derivatives, hydrides of light-weight metals, and especially, liquid hydrogen. The correspondingly highly reactive oxidizers such as the interhalogens (i.e., chlorine trifluoride), liquid fluorine, and certain of its oxides, combine with the propellants to bring specific impulses up over 300 seconds.

The new oxidizers are extremely reactive substances and pose, for the present at least, even greater operational difficulties than the new "exotic" fuels. Ozone is potentially attractive for use in fuel systems,

but techniques to cope with its tremendous instability have not yet been mastered.

Although the chemically fueled boosters that have been used in the past will continue to be the workhorses of the space program for some years to come, NASA is researching other types of propulsion systems—solid, nuclear, and electric. NASA's chemical propellant needs, meanwhile, have mushroomed; for the manned lunar program alone, propellant needs already have dwarfed all previous space requirements. A single Saturn I firing requires 268,000 pounds of RP-1, 694,000 pounds of liquid oxygen, and 16,700 pounds of liquid hydrogen, a total of 978,700 pounds.

At one time, mention of some of these fuels and oxidizers was frightening to chemical and ground support equipment designers. But now, with a wealth of information on the properties of the more hazardous fuels and oxidizers available, and with improved techniques for handling and storing them, commercial application of these materials is more likely.

The increased demand for liquid oxygen in space work, which reduced its cost, has brought about rapid progress in simplifying its storage, handling, and usage. Liquid nitrogen, a byproduct in the manufacture of liquid oxygen, also has become less expensive and has been utilized more routinely in industrial applications requiring inert atmospheres. The manufacture of semiconductor and superconductor materials, for example, requires extensive amounts of liquid nitrogen.

This report on the handling of hazardous materials, therefore, is designed to encourage the best possible industrial utilization of output from the present space effort.

This report, however, is not a handbook giving complete information on each topic. Since more up-to-date information on some chemicals is becoming available, it merely lists and describes each material and provides information regarding its dynamic handling and utilization. Further advances were being made while these pages were being written, and some parts of this publication are certain to seem obsolete to workers in the fields covered.

Dynamic handling, as opposed to static handling (storage), embraces the complex matters of transporting, transferring, mixing of materials, etc.—all the handling functions as the material is drawn from its storage facility to the point where it is introduced into a vehicle. Topics discussed in this report include the properties of such liquid propellants (fuels and oxidizers) as hydrogen, pentaborane, fluorine, and chlorine trifluoride, ozone, nitrogen tetroxide, and hydrazines, and some work on fire extinguishment. Bibliographies of NASA-generated research reports are provided so that the interested person may look more deeply into the work.

Liquid Hydrogen

INTRODUCTION

Of all the desired characteristics of a rocket fuel or propellant, probably the most important are heat of combustion and specific impulse. Liquid propellants exhibit a wide range of capability in these areas. For example, RP-1 (a refinement of kerosene) has an energy level rating of around 20,000 Btu's per pound, and when efficiently combined with liquid oxygen, provides a specific impulse of just under 300 seconds. Being rather easy to handle, and posing few cost and availability problems, RP-1 has been the most commonly used fuel in NASA's Atlas booster program. During the last 25 years, however, much research has been allocated to the study of certain fuels that can deliver energy level and thrust characteristics of more than 20,000 Btu's per pound, and specific impulses, of over 300 seconds.

On the upper extreme, liquid hydrogen can deliver over 50,000 Btu's per pound plus up to 400 seconds specific impulse, almost the theoretical maximum levels. Within the last few years, the decision has appropriately been to begin at the high level with hydrogen. This is evidenced by the development of three hydrogen-burning engines: the RL-10 (15,000 pounds-thrust), the J-2 (200,000 pounds-thrust), and possibly later the M-1 (1,200,000 pounds-thrust). The successful use of liquid hydrogen and liquid oxygen in the RL-10 engine clusters on the Centaur and the Saturn I upper stage launch vehicle has demonstrated both the feasibility and the value of liquid hydrogen.

Consumption of liquid hydrogen has mushroomed from a level of 6 million pounds in 1961 to a projected total of 25 million pounds by 1966. Its utilization has been made more feasible, not by diluting or neutralizing the fuel, but by new developments in hardware and handling.

The commercial importance of gaseous hydrogen has also increased rapidly. A few decades ago the only uses for gaseous hydrogen were for filling balloons, for oxyhydrogen blowpipes to work metals, and

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for producing the theater's "limelight." Today, however, hydrogen is used:

1. In the manufacture of ammonia, useful in many ways, but chiefly for the production of fertilizers.
2. As a "hardener" for certain vegetable and animal oils such as cottonseed oil, so that these oils may be converted into solid or semisolid fats for use in foods, and in the manufacture of soap.
3. For the hydrogenation of coal, to convert it partially into lubricating oils, gasoline, and other products.
4. In the manufacture of methyl alchohol.
5. To provide a reducing atmosphere for furnaces for annealing and deoxidizing brass.
6. In electric arc furnaces to prevent the oxidation of tungsten and molybdenum wire.
7. As heat exchanger medium to cool large electric generators and transformers.
8. For uncounted laboratory purposes.

The volume of the world's annual consumption of pure hydrogen is estimated at many times that of the consumption of purified oxygen.

Non-space applications of liquid hydrogen are still limited, but possibly in the future a user or transporter of bulk hydrogen may find it more economical to handle the material as a liquid than as a high pressure gas. For example, a shipment of one 100-liter dewar of liquid hydrogen (weighing 300–400 pounds) can provide 3,000 standard cubic feet of gaseous hydrogen. In gaseous terms, this would require 15 bottles pressurized to 1,800 psig, each weighing more than 150 pounds. This chapter was written with the increased utilization of liquid hydrogen in mind.

SOURCE AND PREPARATION

Pure hydrogen gas was generated for commercial consumption even before 1900, chiefly by the electrolytic processes. Five methods (plus other processes of which hydrogen gas is a byproduct) are now used to meet the heavy demand for the gas.

During the past few years, more hydrogen has been produced by reacting hydrocarbons, mostly natural gas, with steam than by all other methods combined. An endothermic process, a reaction of steam with desulfurized propane (or methane) in the presence of a suitable catalyst, delivers pure hydrogen with carbon dioxide as a byproduct.

Second in quantity of hydrogen produced is the water-gas catalytic method whereby water-gas (a mixture of hydrogen and carbon monoxide) and steam are reacted catalytically to produce hydrogen, plus

carbon dioxide as a byproduct. It is evident, therefore, that water (in the form of steam) is a chief constituent for the making of hydrogen, the ninth most abundant element in the earth's crust.

Liquid hydrogen is obtained by making use of the Joule-Thomson effect. Similarly, this Joule-Thomson effect is incorporated in the Linde and Claude systems for the manufacture of liquid oxygen and liquid nitrogen from air. The liquefaction process requires highly compressing and cooling the gas in a heat exchanger and expanding it through a valve or orifice. Hydrogen gas is peculiar in that it must be precooled to below its inversion point, $-92°$ F, or the final expansion step will *raise* rather than lower the temperature.

Since low-temperature technology is rapidly developing, new methods of liquefaction may well be forthcoming. This prospect, along with recent improvements in handling, and storage, and new developments in hardware, indicates that the use of liquid hydrogen may become simpler and safer and therefore much more adaptable in the field.

As a propellant combination, hydrogen-oxygen is relatively inexpensive. Liquid hydrogen costs vary, but average near $0.50 per pound; liquid oxygen, $0.02 per pound. The bulk cost of the propellants used in combination averages about $0.10 per pound.

NATURE OF THE HAZARD

Hydrogen, H_2, exists in two molecular modifications, orthohydrogen (nuclei spin in the same direction), and parahydrogen (nuclei spin in opposite directions). At ambient temperature, hydrogen gas is 75 percent orthohydrogen and 25 percent parahydrogen. The equilibrium composition of the liquid hydrogen at the boiling point is 99.79 percent parahydrogen and 0.21 percent orthohydrogen.

Spontaneous conversion of orthohydrogen to parahydrogen will take place until equilibrium is reached, and a large energy differential between the two molecular modifications is released in the form of heat as a result of the conversion. This heat release can cause considerable loss of liquid through boil-off. To avoid the loss, it is imperative to obtain the para form early in the production cycle. This may be effected by the use of certain catalysts.

PHYSICAL PROPERTIES

Liquid

Melting point at atmospheric pressure, °F_____ -434.6
Boiling point at atmospheric pressure, °F_____ -422.9
Critical temperature, °F_____ _____ -400
Critical pressure, psia_____ 191

PHYSICAL PROPERTIES—Continued

Liquid

Specific gravity (liquid water = 1.00)	0.07 (4.37 lbs/ft^3)
Density (liquid), lb/gal (at −422.9° F + 30 in. Hg)	0.583
Specific heat, Btu/lb-°F	0.57
Viscosity (at normal b.p.), poises	182×10^{-6}
Heat of fusion, Btu/lb	25.2
Inversion point, Joule Thomson	−92° F
Heat of vaporization (nearly all para), Btu/lb	190.5

Gas

Specific gravity 68° F (air = 1.00)	0.06953
Density, lb/ft^3 (60° F and 30 inches of Hg)	0.00532
Specific volume, ft^3 lb. (60° F and 30 inches of Hg)	187.9
Gross heat of combustion, Btu/ft^3 (incl. latent heat energy of steam)	325.1
Gross heat of combustion, Btu/lb. (incl. latent heat energy of steam)	61,084
Btu/ft^3 of gas/air mixture (F/A ratio, 0.420 vol., 0.020 wt.; or 28.7% H$_2$ by vol.)	81.3
Ft^3 of air required per ft^3 of combustible	2.382
Pound air required per pound combustible	34.226
Flame temperature (F/A ratio 0.462 vol. 0.0313 wt.; or 31.6% H$_2$ by vol.), °F	3,700
Ignition temperature in air (auto ignition), °F	1065
Ignition temperature in oxygen, °F	1040
Flammability limits, % vol. H$_2$ in air	4.1–74.2
Flammability limits, % vol. H$_2$ in oxygen	4.6–93.9
Detonation limits, % vol. H$_2$ in air	18.3–59
Detonation limits, % vol. H$_2$ in oxygen	15.0–90
Nonflammable limits, air-hydrogen-carbon dioxide	Less than 8% O$_2$
Nonflammable limits, air-hydrogen-nitrogen	Less than 6% O$_2$
Emissivity of flame (blackbody = 1.00)	0.085

CHEMICAL PROPERTIES

Hydrogen in liquid or gaseous form will react violently with strong oxidizers such as oxygen and spontaneously with fluorine and chlorine trifluoride.

Hydrogen gas is colorless, odorless, non-toxic (though asphyxiating), and non-corrosive. When its temperature is that of the ambient air, its density is only about 1/14 of the air density, and the gas is thus strongly buoyant; however, the vapor at the boiling point is as heavy as air at 70° F.

Liquid hydrogen is a transparent, colorless liquid of low viscosity. It does not form solutions with any material except, to a slight extent, with helium. In particular, gases like oxygen and nitrogen condense and freeze to solids in liquid hydrogen without entering into solution. At about 14° K (−435° F) liquid hydrogen freezes to a solid. The temperature and pressure at the triple point (at which solid, liquid

and gaseous hydrogen co-exist) are 14.0° K and 0.071 atmospheres for normal hydrogen, and 13.8° K and 0.069 atmospheres for para-hydrogen. Solid hydrogen freezes into a white crystalline or snow-like mass.

Hydrogen diffuses approximately 3.8 times faster than air. A spill of 500 gallons of liquid hydrogen on the ground has diffused to a non-explosive mixture after about one minute. Air turbulence increases the rate of hydrogen diffusion.

Hydrogen in both the liquid and gaseous states is particularly subject to leakage because of its low viscosity and low molecular weight. Leakage is inversely proportional to viscosity. Because of its low viscosity alone, the leakage of liquid hydrogen will be roughly 100 times that with JP-4 fuel, 50 times that with water, and 10 times that with liquid nitrogen. Likewise, the leakage of gaseous hydrogen will be greater than that for air.

COMBUSTION

Active interest in the science of "fire" began over 300 years ago, but only within the last few decades has some form of understanding been able to qualify, somewhat, the term "combustion." It has been defined as the rapid high-temperature oxidation of fuels. Most fuels at present consist of carbon and hydrogen; as a result, "burning" involves the rapid oxidation of carbon to CO or CO_2, and hydrogen to water vapor. The combustion reaction normally takes place in the gaseous phase, except for the burning of fixed carbon in solid fuels.

To better understand the mechanics of combustion, some terms need discriminative definitions:

1. Flame—a gas rendered luminous by the liberation of chemical energy.
2. Flame front—the surface or area between the luminous region and the dark region of unburned gas found in all gaseous combustion reactions.
3. Burning zones (luminous and reaction)—ignition and most of the oxidation occur in the reaction zone; completion of the burning and emission of light occur in the luminous zone.
4. Stationary flames—the flame front is more or less stationary in space; the unburned gases flow toward the reaction zone at a constant speed. The fuel is either premixed with an oxidizer, or fuel and oxidizer enter the area separately.
5. Explosion flames—explosive burning occurs in homogeneous mixtures of fuel and oxidizer, and the flame front progresses rapidly through the mixture.
6. Detonation—a special type of explosion implemented by a shock wave (pressure) coupled with a reaction zone traveling

through a combustible material at an extremely high velocity. Detonations, a most destructive form of energy release, may · occur in solids (TNT), liquids, or gases.

Detonations occur most readily in a gaseous mixture when it is confined by walls. Some mixtures will not detonate if they are completely in the open. Studies show that hydrogen-*air* mixtures *do not* go through a transition from ordinary flame to detonation wave under such circumstances, *unless* the ignition source imparts considerable extra energy in the form of a shock wave. A blasting cap will cause a short-lived detonation to occur in hydrogen-air mixtures.

Hydrogen-*oxygen* mixtures, on the other hand, *will detonate when unconfined if ignited by even a small, invisible spark.* It is not possible to state positively the degree of confinement required to permit detonations to form in hydrogen-air mixtures. It is known that the "one-wall" case—that is, burning about the ground—does not cause detonation. It is also known that the four-wall case—that is, a U-shaped bay on the ground—will permit detonation. Pending further data, a storage vessel protected by a single barricade is considered unconfined.

IGNITION

When mixed with air or oxygen over a wide range of proportions, hydrogen gas forms a highly flammable mixture. Ignition may result from a low energy input, possibly one-tenth that required to ignite a gasoline-air mixture.

Temperatures of about 1,000° F are usually required for the ignition of hydrogen and air or for oxygen mixtures. However, at less than atmospheric pressure, i.e., at 2/10 to 5/10 atmosphere, ignition will occur if temperatures as low as about 650° F are maintained long enough. While normal deflagrations of hydrogen-air mixtures have flame speeds of about 30 feet per second, the flame speeds during detonation are of the order of several thousand feet per second. Flame envelops the mixture almost instantaneously. For normal combustion the pressure rise ratio is approximately seven, while for detonation the pressure rise may be as much as twenty times the initial pressure. The rate of pressure rise is so great that it has the destructive characteristics of dynamite explosions. As long as hydrogen-air mixtures are unconfined, detonation is not very likely to occur unless the ignition source is very large. On the other hand, ignition of a partially confined mixture will very likely cause detonation.

Vents from liquid hydrogen storage dewars may be stopped by accumulations of frozen moisture condensed from the air. A resulting pressure build-up can be sufficient to rupture the container and release a quantity of hydrogen. An explosion may be caused by a spark or heat generated by the rupture.

Liquid hydrogen is subject to contamination by condensed and so-lidified air obtained from the atmosphere or from accumulation of traces introduced in manufacture. This mixture is unstable and may explode.

Experiments have provided a good basis for fixing quantity-distance relations in storage areas where free air is the only oxidant present. The following facts are important:

1. Detonation does not occur in the mixtures formed from liquid hydrogen vaporizing into air as long as the mixtures are unconfined.
2. The pool burns steadily in a column that is vertical in still air and of the same diameter as the pool.
3. Compared to ordinary fires, hydrogen fires do not heat nearby objects by radiation to any great extent. Nor do hydrogen fires last long, since the liquid evaporates quite rapidly.
4. Flames of diluted hydrogen-oxygen mixtures such as hydrogen and air are almost invisible. Only the impurities burning in the flame are visible.

Other "oxidizers" capable of forming explosive or flammable mixtures with hydrogen are chlorine and fluorine.

TOXICITY

Hydrogen gas is non-toxic, but can cause asphyxiation by diluting air enough to exclude oxygen. Due to its high heat conductivity relative to air, hydrogen gas can actually be sensed by skin contact. Severe burns have been suffered by persons exposed to hydrogen flames from the ignition of hydrogen gas escaping from small leaks in laboratory apparatus. As a result, people have died from exposure to rather small local flash fires from the ignition of gas produced by the evaporation of small amounts of liquid hydrogen. All the hazards when gaseous hydrogen is present are equally serious with liquid hydrogen because of the ease with which the liquid evaporates.

Liquid hydrogen, as a cryogenic liquid, remains a serious hazard by virtue of its low temperature. If it comes in contact with the skin, it can cause a serious burn. Although danger of contact with liquid hydrogen from open vessels or leaky hoses is unlikely, splashing could occur and be a real hazard.

DYNAMIC HANDLING

Until a few years ago, liquid hydrogen was more or less a laboratory curiosity and had been handled delicately in small quantities. Even as a top contender for missile and booster fuel, liquid hydrogen until recently was considered almost too hazardous to use because of three chief properties: its low ignition-energy requirement when mixed

with air, its wide limits of flammability, and its known detonation effects under confined conditions.

During the last few years, various studies in the peculiarities of liquid hydrogen and the resultant creation of bulk liquid hydrogen storage and handling facilities have revealed that the hazards are apparently not so great as had been suspected. Hydrogen's chief advantages are its lack of toxicity and its non-corrosion characteristics. The effect of liquid hydrogen flame radiation intensity on workers in the areas is less than that for hydrocarbons. The chance of detonating a large mass of hydrogen released by accident is quite low because of the improbability of both a stoichiometric mixture with air being produced and a strong enough shock being present to initiate detonation. On the other hand, handling personnel who have fallen victim to hydrogen-fueled conflagrations are not likely to appreciate the "comparative" factors. The nature of hydrogen as a hazard is reputable, indeed, and, as described in the previous section, the dangers involved in hydrogen handling are sufficient to demand the utmost in both precautions and preventive design efforts.

MATERIALS AND DESIGN

Metals

In the past, the austenitic (300 series) stainless steels have been used most extensively with liquid hydrogen. They remain ductile at cryogenic temperatures, and their coefficients of thermal expansion and thermal conductivities are relatively low. Types 304, 304L, 308, 316, 321, and 347 are examples of commonly used stainless steel materials. Any materials welded should be subsequently heat treated to avoid embrittlement.

In addition, aluminum, copper, monel, and inconel are permissible construction materials for use in liquid hydrogen systems. The actual selection of materials should evolve around the specific design application, with consideration of thermal conductivity, strength, porosity, weight and cost.

Contact of dissimilar materials in liquid hydrogen systems or containers should be avoided; galvanic corrosion could result in leaks. Furthermore, materials of unequal coefficients of thermal expansion might cause leakage at connection points, or within seals of certain components.

Non-metals

Teflon (polytetrafluoroethylene) or Kel-F (polytrifluorochloroethylene) can be used in liquid hydrogen systems. Asbestos impregnated

with Teflon and Nylon have also been mentioned. Some recommended uses are:

1. Valve seats (Kel–F is preferred) for service to 300 psig; the seat must be shrouded on three sides to avoid plastic flow.
2. Soft coating on metallic O-rings to provide more positive seal.
3. Flat-thin gaskets for tongue-and-groove type flanges where the gasket is shrouded on four sides.
4. Spacers in vacuum area between liquid flow tube and vacuum pipe.
5. Gland packing or seal *only* if it is maintained near ambient temperature as in an extended bonnet of a shutoff valve. The contraction or shrinkage of Teflon when cooled from ambient to cryogenic temperatures allows leakage.

For gaseous hydrogen at ambient temperature, the *valve seal materials* can be conventional composition type.

For *valve seat materials* on *liquid hydrogen systems up to 300 psig*, Kel–F is first choice and Teflon second. Kel–F has a higher tensile strength and is less brittle at cryogenic temperature. Both should be shrouded to avoid plastic flow. Valves for liquid service over 300 psig should have metal-to-metal seats because the pressure requires excessive seating force for the Kel–F and Teflon.

Hardware	Liquid Hydrogen Service	Gaseous Hydrogen Service
Valves	Forged 304 stainless steel or brass body with extended bonnet.	Conventional material commensurate with pressure requirements.
Fittings	Stainless steel bayonet type for vacuum jackets.	Conventional material commensurate with pressure and sealing requirements.
O-rings	Stainless steel type (or Kel-F).	Rubbers, silicones, elastomers, etc.
Gaskets	Soft aluminum, lead or annealed copper between serrated flanges.	Conventional material commensurate with pressure and sealing requirements.
Hoses	Flexible type 316 stainless steel.	Aeroquip 1508 (outside), Mil-H-8794 (inside).
Burst disc assembly	304 or 304L stainless steel flanges.	Forged steel flanges.
Tubing	304 or 304L stainless steel.	Uncoated wrought steel or any 300 series stainless.
Dewars	304 or 304L stainless steel.	

Tubing and Fittings	Maximum Size	Pressure Limit
STEEL AND STAINLESS STEEL FITTINGS		
Flareless	¼ inch	Tube strength with proper safety factor.
Flared	1 inch	Tube strength with proper safety factor.
Flared	1½ inches	125 psig.

NASA uses flanged or welded joints for steel tube sizes greater than 1 inch and pressures greater than 125 psig.

It may be desired to use flared fittings in some cases involving pressures higher than 125 psig and tube sizes larger than 1 inch, but such use is not recommended.

Tubing and Fittings	Maximum Size	Pressure Limit
ALUMINUM FITTINGS		
Flareless	Not approved	Not approved.
Flared	⅜ inch	Tube strength with proper safety factor.
COPPER-BASE FITTINGS AND ALUMINUM FITTINGS		
Flareless	Not approved	Not approved.
Flared	Industrial	Tube strength with proper safety factor.

Limitations

There are other limitations on fittings as a result of fire hazards for hydrogen, oxygen, and hydraulic systems. Aluminum or copper would melt and release the hydrogen, only to increase the extent of the damage. Only stainless steel is recommended. Of course, for specific applications such as heat exchangers in research apparatus other materials may be required.

Allowable Stresses

For liquid or gaseous systems, the design stress for vessels or tubing must not exceed 50 percent of the minimum yield of the material at 70° F.

Thermal Contraction

Thermal contraction of a liquid hydrogen system of stainless steel is usually calculated from ambient to minus 420° F as 0.35 percent of the original length. Long runs of piping require a support at intervals to allow for the axial motion, with lateral and/or vertical motion restrained.

Fabrication Methods for Fused Joints

General.—The fused joint, because of its simplicity and high reliability, finds many applications in both gaseous and liquid hydrogen systems. Soft soldering, hard soldering, and welding can often meet the bonding requirements; however, for safety reasons the welded joint takes first preference and in numerous cases is mandatory. In addition to the high structural efficiency and fatigue resistance of a properly executed weld, it is often the only fused joint that has a melting point substantially equal to that of the bulk structure. This is a potent safety factor where, in the event of an accidental fire, a melted joint could release additional large quantities of fuel. In large systems, such failures could lead to a chain-reaction catastrophe. For this reason all general purpose liquid or gaseous hydrogen systems should be constructed of high melting point materials.

Soft Solder Joints.—Soft solder joints must be confined to noncritical locations, such as instrumentation wiring and system assembly, where a failure will not result in a hazardous condition. At temperatures below about 0° F, pure tin sometimes undergoes a crystalline phase change and transforms to "gray tin." The "gray tin" loses all structural integrity and crumbles. Experience has shown that solders containing at least 60 percent lead give satisfactory results in cryogenic service. It is believed that the normal impurities in the commercial solders plus the solution of metals from the parts being joined greatly enhance the structural performance of the solder joint. Because of the undesirable properties of tin at low temperature some people have specified solder composed of 95 percent lead and 5 percent silver.

Silver Solder Joints.—NASA has encountered no unique problems with these materials. The choice of solder composition is determined by its ease of application to the material to be joined. Silver solders are recommended for joining copper base materials and for joining dissimilar metals such as copper to stainless steel.

Welded Joints.—Welding is the first preference for all hydrogen systems; all forms of welding can be used. The type of weld used is generally determined by factors other than the use of hydrogen. Heli-arc is generally preferred for joining light gauge stainless steel and is often preferred for construction of vacuum jacketed equipment.

Conventional arc techniques are also used extensively, especially for heavy gauge material where cost is a strong factor. Filler material, and stress relieving requirements are determined by the parent material and normal standard practices should be followed.

TRANSFER

Personnel Protection

Handling personnel should wear protective face shields, goggles, and special clothing. Gauntlet-type gloves or clothing which would hold liquid against the body must be avoided. Donning synthetic clothing, such as Nylon, and non-conductive shoes *must be avoided* because of the ease of generating static electricity.

Fuel and Fuel System Contamination

Explosions in pipes carrying liquid hydrogen have been attributed to electrical discharges generated by the shearing of frozen particles of oxidant in the stream.

When water vapor is mixed with liquid hydrogen, small, abrasive ice crystals are formed that can cause immediate galling of rubber surfaces. This would be detrimental to valves and components. A cleaning process should be used to remove greases, etc., which could solidify and flake off when cooled.

Foreign material in hydrogen systems which could cause valves, etc., to malfunction or could generate static electricity, should be removed before placing the system in operation.

Purging

Prior to the introduction of liquid hydrogen into a storage container, transfer line, or system, the system must be thoroughly purged of:
1. Combustible mixtures within the system.
2. Contamination of hydrogen.
3. Gases which may freeze into particles.
4. Combustible mixtures which form upon dismantling the system.
In order to avoid dangerous mixtures:
1. Purge air from a system to receive hydrogen and,
2. Purge hydrogen likewise from a system to receive air.
Purging may be accomplished with inert fluids such as nitrogen, carbon dioxide, helium, or water, if the fluid is compatible with the low-temperature situation.

Because of its scarcity, *helium should be used only where absolutely necessary*. The use of liquid nitrogen is a logical step in the purging process. Water provides a convenient medium for purging vent lines containing air or gaseous hydrogen.

Purging of air with hydrogen or purging of hydrogen with air both involve a combustible mixture and should be allowed only in relatively small, simple systems capable of withstanding a detonation.

Cooling-Purging Method

Cooling-purging procedures must be followed prior to filling a vessel with liquid hydrogen:

1. Evacuate the vessel or system to approximately 1 cm of mercury.
2. Introduce the liquid nitrogen into the vessel or system, taking care to insure that there is no air migration which would cause contamination.
3. Allow ample time to obtain all of the cooling possible from the liquid and cold gas.
4. Drain off the remaining liquid nitrogen.
5. Remove the nitrogen gas atmosphere by evacuating the vessel or system to 1 cm of mercury.
6. Introduce the hydrogen purge gas slowly. Continue the flow until the vessel or system goes to a slight positive pressure.
7. Admit the liquid hydrogen into the vessel or system.

Upon shutdown, systems should be purged after use periods, or for the following reasons:

1. Alteration or repair of the system.
2. Presence of personnel in the vicinity of the system for more than a short period.
3. A shutdown for more than a short period.
4. Absence of attendant for more than a short period.

Disposal

Burning disposal of larger quantities of hydrogen than can safely be handled by roof vent systems is probably best handled in a "burn-off" system in which the liquid or the gas is piped to a remote area and burned with air in a multiple burner arrangement. Such systems are operated with pilot ignition means, warning systems in case of flame-out, and means for purging the vent line. Attention should be given to the stress, the thermal contraction, and the support of the long pipe lines involved, to the removal of ignitable substances in the vicinity, and to hazards to low-flying airplanes.

HAZARD CONTROL

Presence of Hydrogen Gas

When an accumulation of combustible gas is known to be present in a test cell or area:

1. *Do not actuate electrical or other devices having questionable non-sparking characteristics.* Much "explosion-proof" equip-

ment as well as telephones and radios belongs in this category when placed in a hydrogen-air atmosphere. Metal dampers; sash, doors, etc., may create sparks when opened.

2. Shut off the gas supply and ventilate.
3. Notify the plant protection organization.
4. Evacuate the area. Personnel must stay out of areas where there are combustible gases.

Fire

Hydrogen fires are invisible. The invisible flames may be many feet long, and may shift quickly with the slightest breeze. Therefore, *personnnel must wear protective clothing in fighting hydrogen fires.*

The only positive way of handling a hydrogen fire is to let it burn under control until the flow of hydrogen can be stopped. If a hydrogen fire is extinguished and the flow of hydrogen is not stopped, a hazardous combustible mixture forms at once. Very probably the mixture will be ignited, explode, cause more damage, and restart the fire.

Although a hydrogen fire should not be extinguished until the flow of hydrogen can be stopped, water sprays, etc., should be used to extinguish any secondary fire and to prevent the spread of the fire. The hydrogen containing equipment should be kept cool by water sprays to decrease the rate of hydrogen leak and prevent further heat damage.

Remote-controlled water-spray equipment is preferrable to hoses to cool equipment and to reduce the spread of the fire. Should the use of hoses become necessary, operating personnel should stay behind protective structures.

Carbon dioxide (CO_2) should not be used on a hydrogen fire because the hydrogen flame temperature is high enough to decompose the CO_2 into CO. The CO is both toxic and flammable. If CO_2 is used on fires which accompany the hydrogen fire, this should be kept in mind, and ventilation should be adequate. Preferably, in the case of a hydrogen fire, CO_2 should be used only out-of-doors.

The standard dry chemicals are preferred to CO_2 because they make the flame visible.

Fire-fighting or other emergency personnel should confer and cooperate with personnel who are familiar with conditions and materials in the area of the emergency. Unexpected conditions may require special actions.

Explosion

If a large liquid hydrogen container or supply piping system is ruptured in such a manner that much hydrogen is released and ignited, hazardous conditions exist because of:

1. *Flame effects.*—Flame will occupy the volume around the ruptured tank. Spills of a few hundred gallons may cause a "flash hot-gas ball" about 100 feet in diameter. Wind may change the shape to an ellipsoid almost entirely downwind of the rupture. Flame temperature will be approximately 3600° F.
2. *Radiation effects.*—The hot gas ball will radiate, but at $\frac{1}{10}$th the rate for gasoline-air fires. Radiation effects on adjacent vessels and lines may not be severe, especially when reflective painting of surfaces is required.
3. *Blast effects.*—Detonation of hydrogen and air in unconfined spaces has not been experienced, but a lower order of explosion, called a deflagration, or flash-fire, may occur. The maximum theoretical over-pressure occurs in the flame zone where the mixture is stoichiometric. Restricted combustion gases can reach 105 psig but in free space over-pressure due to blast effect will be below the theoretical maximum for confined gases.

Hydrogen systems must be designed and installed to *fail-safe* in case of failure of utilities or of other services. The hazards of momentary power or other service failure should be examined. Generally, automatic reset devices should be avoided. The use of reset and non-reset devices in the same setup can lead to unsafe conditions.

As a general policy, a sufficient number of safeguards must be provided in a test facility to avoid a catastrophe if the operating personnel should err in operating procedures.

STORAGE AND USE

Storage Containers

Liquid Hydrogen.—To minimize evaporation loss, liquid hydrogen is stored out-of-doors in dewars. Generally, dewar construction consists of a stainless steel tank within a vacuum jacket (double-walled). Some dewars have the vacuum jacket filled with "Perlite," a white powdery insulation. The "Perlite" reduces shell radiation and serves to reduce heat transfer in case of loss of vacuum. If liquid nitrogen jackets are used, the nitrogen jacket must be equipped with a proper relief valve, burst disc, and venting. Sizes of dewars available at Lewis vary from the 25-liter portable type to the 6,000-gallon mobile trailer.

Gaseous Hydrogen.—Large volumes of gaseous hydrogen are stored out-of-doors in mobile tube trailers of approximately 70,000 standard cubic feet capacity. The maximum pressure is about 2,400 psig. Small volumes of gaseous hydrogen are stored and transported in

portable cylinders of approximately 200 standard cubic feet capacity. The maximum pressure is about 2,100 psig.

Protection of Dewars.—All dewars must be protected from shrapnel. Barricades should be installed near the test rig to protect the dewar, because blast fragments or disintegration of high speed machinery could be hazardous. In the case of a high rotational speed test rig, the housing may be designed as the shield between the rig and dewar.

Pressure Relief Devices.—All pressure vessels should be equipped with burst diaphragms set for a pressure 25 percent above the maximum design working pressure. The burst disc housing should be located so that its temperature does not vary appreciably, and its material and design should be selected according to temperature. (A relief valve, set to not more than 10 percent above the maximum working pressure of the vessel, may be installed in parallel with the rupture disc.) The outlet of the burst diaphragm (and/or relief valve) should be ducted away from the work area in the same manner as the tank vent lines.

Gaseous Hydrogen Transfer Connections.—Gaseous hydrogen trailer connections to rigidly mounted test cell piping must use weather-proof, flexible high-pressure hose. Hose lengths exceeding 6 feet are not recommended. Furthermore, lengths over 2 feet should have anchor cable, with support clamps at intervals of 2 feet or less, to keep any broken hose from whipping.

To prevent infiltration of air the cylinder pressure should not be below 10 psig.

USE CONSIDERATIONS

Hydrogen operations are safest when conducted out-of-doors where hydrogen leaks are easily diffused and rapidly diluted to non-combustible properties. However, if protection from the weather is required, the order of preference of building types is as follows, with minimum enclosure or confinement the rule:

1. Roof without peaks or sides (where warmed hydrogen gas could accumulate).
2. Well ventilated roof with removable sides.
3. Well ventilated "expandable" building.
4. Well ventilated permanent building.

Only non-combustible materials should be used for building or equipment construction. If an enclosure must be totally confining, a non-frangible area is desirable. For example, window panes should be made of plastic, not glass, and hinged to swing outward in the event of an explosion. But the hydrogen bulk storage area should be out-of-doors and sufficiently remote so that any leak would not migrate into any building

It is advisable that a pill box type control room be located away from the hydrogen test area or work area. This control room must be designed so that no hydrogen can enter by means of either piping or conduit.

Any area containing hydrogen system components should be well ventilated with quantities of air sufficient to prevent an explosion by diluting any escaping gases.

Means should be provided for detecting the presence of free hydrogen in all areas in which there is a possibility of a hazardous accumulation. Because hydrogen is both odorless and colorless, it cannot be detected by odor or vision. The cloud of frozen air and water which accompanies leaks is visible, but detection of leaks by observation of such clouds may not be reliable because clouds of water vapor also rise from cold exposed surfaces when no hydrogen leak is present. To avoid a hazardous accumulation, detection equipment is advisable to provide rapid and immediate response.

The manual use of commercial portable detectors in an area contaminated with hydrogen can be hazardous and should be discouraged. If deemed necessary and reasonably safe, the detectors should be used with a probe that can be extended in front of the user.

Presence of Personnel in Test Rooms.—The chief hazards to both personnel and equipment arise from fire, explosion, and rupture of pressure vessels. Additional hazards to personnel might arise from freezing and suffocation.

Every entrance into an operating test cell must be considered dangerous. Entrance into such an area should be made only after the severity of operating conditions has been reduced. Cells or areas filled with combustible mixtures should not be entered.

Attention should be directed to the ventilation, or source of oxygen, for control rooms in case the control room should be enveloped in combustibles or products of combustion. Inert gases under pressure should not be piped into control rooms if there is a possibility of either accidental release or suffocation.

QUANTITY-DISTANCE RELATIONSHIPS

Two different situations must be considered in connection with quantity-distance relations:

1. The *storage* of liquid hydrogen.
2. Its *use* in pressurized propellant tanks.

Storage Areas

Simple quantity-distance relations can be stated for storage areas which differ slightly, depending on the shape of the vessel used, as a result of the different radiation-receiving properties.

For spherical tanks of:

1. Less than 5,000 pounds per tank, 35 feet between tanks.
2. More than 5,000 pounds per tank, 50 feet between tanks.

For cylindrical tanks of:

1. Less than 5,000 pounds per tank, 40 feet between tanks.
2. More than 5,000 pounds per tank, 60 feet between tanks.

The following storage conditions must also be met:

1. Storage vessels must be in the open and unbarricaded.
2. Dikes must be provided to prevent spilled liquid from carrying a fire to nearby tanks. (Note: In parking areas for transport dewars, when diking is not required, such areas should be chosen so as to take advantage of slopes, drainage ditches, etc., to lead spilled liquid away from adjoining dewars.)

The use of barriers for protecting dewars is of questionable value because:

1. Barriers tend to confine combustibles.
2. Barrier walls provide surfaces which may enhance the possibility of detonation.

Transfer Areas

In use areas the *liquid hydrogen will be under pressure and in more or less close proximity to oxidizers* (e.g., liquid oxygen) at least while tests are in progress. Safety problems in use areas are more severe than in storage areas, and there is as yet very little test information to help decide quantity-distance relations.

One problem is that any rupture while the system is pressurized will eject the liquid rapidly and with energy for mixing. Furthermore, ejection might well be into the air where conceivably very large clouds of flammable mixture might form.

Another and more serious problem is that both liquid hydrogen and oxidizer, for instance, liquid oxygen, may be spilled. It is known that gaseous hydrogen-oxygen mixtures will detonate in open, unconfined spaces; furthermore, liquid hydrogen and solid oxygen will detonate under some conditions.

In view of the greater hazards in use areas as compared with storage areas, it must ordinarily be assumed that detonations may occur. Quantity-distance relations suitable for high explosives such as TNT must be adopted.

Until further evidence becomes available, the "TNT equivalent" of liquid hydrogen may be determined as follows:

1. Calculate how many pounds of stoichiometric hydrogen-oxygen or hydrogen-fluorine mixture could be formed in the maximum

foreseeable accident. Multiply by 0.65 to account for mixing inefficiency.

2. Since each pound of such mixture is equivalent to 1.3 pounds of TNT in the blast-wave pressure it can produce, multiply the number obtained above by 1.3.

The following table may now be entered with this quantity to determine the appropriate distance.

Table of Safe Distances*

Liquid Hydrogen Use Areas Where Oxidizers Are Present

TNT Equivalent, pounds		Safe Distance, feet
Over	Not Over	
0	50	300
50	100	380
100	200	470
200	300	540
300	400	590
400	500	640
500	600	680
600	700	700
700	800	750
800	900	780
900	1,000	800
1,000	1,500	920
1,500	2,000	1,010
2,000	3,000	1,160
3,000	4,000	1,270
4,000	5,000	1,370
5,000	6,000	1,460
6,000	7,000	1,540
7,000	8,000	1,600
8,000	9,000	1,670
9,000	10,000	1,730

*Armed Services Explosives Safety Board, Dec. 1955.

The distances shown in this table are sufficient to prevent danger to personnel from the direct blast, and to prevent appreciable damage to structures. "Appreciable damage" means removal of roofing or siding, collapse, or deformation of structural members in buildings of ordinary construction designed to bear the usual wind and snow loads.

It may be noted that nothing has been said about the *TNT equivalent of hydrogen-air mixtures*. In use areas, where hydrogen is being used as a working fluid, as in pump tests, there is the chance that some or

all may escape and mix with air. As has already been pointed out, unconfined hydrogen-air mixtures do not detonate; nevertheless, there is ample evidence that large clouds can burn with an explosive type of energy release, producing destructive pressure waves. Unfortunately, there have not yet been any studies of the relation between the amplitude of the pressure wave, and the size and composition of the unconfined burning cloud. Thus, nothing quantitative can be said at present, pending experiments and/or experience with this type of explosion.

ELIMINATING IGNITION SOURCES

Even with the best of hydrogen containment efforts, accidental leaks and accumulations may occur.

Therefore, *the policy is to eliminate likely ignition sources or place them away from the hazard area.*

If ignition sources are a required part of a hydrogen test, provision should be made so that any explosion or fire will occur within certain desired safety limits.

Potential Ignition Sources

Friction Sparks.—Friction sparks are caused by hard objects coming into forcible contact with each other; that is, metal striking metal, metal striking stone, or stone striking stone.

A friction spark is a particle of burning metal which has been sheared off as a result of contact. Initially, the particle is heated by mechanical energy of friction and impact converted into heat. The freshly exposed surface of the particle may oxidize at the elevated temperature to cause an increase of temperature until the particle is heated to incandescence.

Sparks struck from hand tools are considered to have low total energy. Sparks from mechanical tools such as drills and pneumatic chisels generate high energy sparks.

Impact Sparks.—Impact sparks are also caused by hard objects coming into forcible contact with each other.

Impact sparks are produced by impact on a quartzitic type rock. Quartz is piezo-electric and can convert mechanical into electrical energy. As in the case of friction sparks, small particles of the impacted material lose heat after the initial impact.

"Spark-proof" Tools.—Tests and experience have shown that so-called "spark-proof" tools are not spark-proof, and do cause ignitions. Further, with hydrogen, the energy required for ignition is so small that the so-called "spark-proof" tools reduce the hazard very little and give a false feeling of security. They are not required.

All tools should be used with caution to prevent slipping, glancing blows, or dripping, all of which would cause sparks.

Spark-proof and Conductive Floors.—These are not required because the same comments apply to them as to "spark-proof" tools. However, if such floors are used, care should be exercised not to destroy the safety properties by cutting the floor or painting with non-conductive paint.

Hot Object, Open Flames, Smoking.—Objects at temperatures of over 1,000° F (or about 650° F prolonged at less than atmsopheric pressure) will cause ignition of hydrogen-air or hydrogen-oxygen mixtures at atmospheric pressure. Hence, care must be taken to protect electric lights which would be ignition sources if broken. Protective fixtures guards should be used, or the electrical circuits de-energized during the times when hydrogen is in the area. Open flames or smoking must not be permitted.

If a test requires the exposure of hot equipment that might ignite escaping hydrogen, provisions must be made so that any explosion or fire will occur safely. *Before welding operations, care must be taken to be sure no hydrogen is or will be in the work area.*

Flame Arresters.—Typical flame arresters of the screen type rely on the fact that a flame will be quenched if sufficient heat can be removed from the gas by the arrester. The quenching distance is the spacing between parallel walls which will just permit a flame to pass. Quenching distance for hydrogen is on the order of $\frac{1}{4}$ that of other fuels. As the pressure increases the quenching distance decreases, so flame may be propagated through insulating material normally capable of snuffing out air-hydrogen flames. *Conventional screen-type flame arresters are not effective in hydrogen vent stacks.*

Sintered bronze flame arresters are effective in stopping hydrogen flames. Porosity, area, thickness, duration of flame, pressure and mass flow are factors that must be considered. Further developments of this type flame arrester are expected.

Sintered stainless steel flame arresters are not as effective as the sintered bronze.

Static Electricity.—Flowing liquid or gaseous hydrogen causes charges of static electricity. The same is true of most liquids or gases.

Turbulence in liquid hydrogen transfer and storage equipment should be avoided as much as possible. For example, liquid falling into a partially filled vessel will create more static charge than if it is piped to enter beneath the liquid surface.

All equipment containing liquid or gaseous hydrogen should be properly grounded to prevent accumulation of a static charge which would cause a static spark.

People generate high voltage charges of static electricity on themselves. Operators must remember to ground themselves before touch-

ing hydrogen couplings and joints to prevent ignitions in hydrogen-air atmospheres.

Electrical Sparks.—Electrical sparks are caused by sudden electrical discharges between objects having different electrical potentials. Breaking electrical circuits, or discharges resulting from static electricity, may carry tremendous amounts of energy but hazardous discharges usually can be prevented by proper grounding.

Static electricity will generate sparks which will ignite a hydrogen-air or hydrogen-oxygen mixture. Static electricity is caused by many typical, difficult-to-avoid situations in everyday life. Non-conductive liquids or gases cause charges of static electricity. Turbulence in containers as well as laminar flow in systems has the same effect.

Therefore, in hydrogen areas where special care must be taken to prevent static sparks from the above or any other sources, the following precautions are mandatory:

1. Ground all metal parts of the test rig and structure enclosing it.
2. Make sure machinery belts are spark-free.
3. Avoid using combs.
4. Avoid wearing nylon or other synthetic clothing.
5. Be sure personnel ground themselves before touching or using a tool on dewars or vents.
6. Keep furred animals out of hydrogen areas.

In spite of precautions, static sparks may occur from unknown sources.

ELECTRICAL EQUIPMENT AND WIRING

Electrical sparks are caused by breaking live circuits, as at switches, commutators, loose connections, or breaking wires. Hot wires or parts are also ignition sources. (See section on "Nature of the Hazard.")

"Explosion-proof" equipment is equipment that is strong enough and sealed tightly enough to contain an explosion caused by a spark within the equipment. However, there is little equipment made which is strong enough to contain a hydrogen explosion. Instead of requiring expensive and complicated "explosion-proof" equipment, the following are recommended:

1. Plentiful ventilation.
2. Electrical installations that are spark and ignition proof, or
3. Sparking or ignition-hazard equipment that is enclosed and pressurized with clean dry air or nitrogen at low pressure to prevent infiltration of hydrogen which would be ignited, or
4. Sparking or ignition-hazard equipment that is placed at a safe distance from the hydrogen area.

In most instances, the above can be achieved by careful selection, installation and use of general purpose electrical equipment.

Conduit.—Threaded, rigid, metal conduit *is not required* except as judged necessary for protection of wiring against mechanical damage. If used, the ends should be sealed if the conduit could conduct leaked hydrogen to a non-hazard area.

Liquid-tight, flexible conduit may be used and the ends sealed as above.

Wiring (Without Conduit).—Flexible heavy-duty rubber-covered cable may be used without conduit. The ends must be sealed, as with cord grips, to prevent hydrogen infiltration.

Starters, Relays, Breakers.—Equipment of this nature must be located remotely from the hazard area, or pressurized, or continuously scavenged of any combustible.

Solenoid Valves.—Solenoid valves, e.g., the Skinner Electric Valve, are considered spark-free and need not be pressurized with inert gas or sealed. If desired, a fuse or other protection may be used to prevent overheating.

Switches.—Switches should be spark-proof or remotely located. A master switch should be used to de-energize all lights in a single room. Receptacles should be de-energized while hydrogen is in the area. Their conduits or cables should be sealed to prevent conducting hydrogen to sparking equipment.

Extension Cords.—Extension cords should be of the heavy duty type to protect against mechanical damage. The cords should contain a ground wire. The ends should be sealed to prevent hydrogen infiltration. Connection devices should be of the twist-lock type.

Seal-offs.—When electrical equipment is totally enclosed and pressurized the electrical conduits should be equipped with seal-offs to prevent the exit of pressurizing gas. Seal-offs are also required in all conduit runs leaving the test cell.

Grounding.—All machinery, metal conduit systems, and control enclosures should be grounded to the building ground or if portable should be suitably grounded (at least at No. 2 AWG flexible ground cable) after being placed in position for test.

Motors.—Motors should be:

1. placed away from the hazard area, or
2. totally enclosed and pressurized, or
3. spark ignition free, or
4. hydrogen explosion-proof.

Three phase induction motors are normally considered spark-free although loose rotor bars and static charges in the rotor can cause sparks.

Single phase motors with starting switches or brushes are not approved since they are spark and ignition sources. Single phase motors without sparking switches (e.g. split-phase type and usually of less than $1/20$ hp) are considered safe.

Frames of motors should be bonded to the conduit system feeding them and thus be grounded.

Lighting Fixtures.—Ordinary light fixtures are not safe. They must not be used when hydrogen is in the area. Light bulbs that screw into sockets may loosen and cause sparks. Vapor-tight fixtures may be used if the hydrogen is normally contained and if plentiful ventilation prevents the accumulation of any hydrogen which may escape.

Instruments.—Instruments should be constructed and installed so that the sensing element, etc., will not produce sparking to ignite a hydrogen-air atmosphere, or they should be totally enclosed and pressurized, or located away from the hazard area.

Telephones.—Telephones should be of the hydrogen explosion-proof type, or located at a safe distance from the hazard area.

Control Circuits.—Control circuits should have low voltage protection type master control switches. Combustible gas and CO_2 protection should be connected to the control circuit ahead of the master control switch. All valves, instruments, and other equipment should be connected on the load side of the master control switch.

Lightning Protection.—Lightning protection in the form of lightning rods and ground rods suitably connected should be provided at all preparation, storage and use areas. All equipment in buildings should be interconnected and grounded to prevent inducing sparks between pieces of equipment during lightning strokes. The area is considered protected if lightning rods are within 30 degrees of either side of the vertical.

RESEARCH NOTES

Early pioneers in the rocket field knew of the advantages of using liquid hydrogen as a rocket or missile fuel because of its most favorable specific impulse characteristics; but the associated handling problems combined with extreme physical properties of the liquid and the gas discouraged its usage. Research devoted to such usage has been intensified recently and such problems appear surmountable now by improving the various techniques of production, handling, and storage.

NASA's Centaur development program, presently underway at the Lewis Research Center, began as a hydrogen technology research program under the Department of Defense in 1958 with a view toward harnessing the high specific-impulse potential of liquid hydrogen as

a fuel. As a result, NASA's Lewis Research Center, with its work .concentrating on space vehicle propulsion and power generation, has become the focal point for major liquid hydrogen research. This chapter is a compendium of Lewis's experience in handling large volumes and thus may be helpful from a practical point of view.

SUPPLEMENTARY DATA

Additional Research on Quantity-Distance Relationships:

Glass Breakage.—The distances referred to on pages 19 to 22 are not sufficient to prevent the two most common kinds of minor damage, namely, cracked plaster and broken or pulled-out windows. Window damage is probably the most persistent complaint. Despite many programs designed to produce quantity-distance relations for glass damage, there is no agreement among the various investigators. This is probably due to the highly variable and directional effects of wind velocity and temperature aloft on the paths of pressure waves, and to the great variations in window size and mountings. Consequently, *the most conservative results* found from various investigations are used here. The following equation will estimate the *extreme* distance at which glass breakage may occur:

$$d = 410 M^{1/3}$$

where,

d = extreme glass-breakage distance, feet

M = TNT equivalent of stoichiometric H_2O_2, pounds

When the quantity-distance table and the glass breakage formula are applied to a given situation, it is clear that there will be a large area in which glass breakage may be expected. It will be necessary to decide in each case whether this damage can be tolerated.

Typical Application of Foregoing Rules:

1. Set-up: LOX-liquid H_2 in flight configuration, one tank mounted above the other; 770 pounds LOX, 136 pounds LH_2. In the maximum accident, both tanks could spill.
2. TNT equivalent: Since 8 pounds of LOX are needed to form a stoichiometric mixture with 1 pound of LH_2, the LOX is in short supply in this case; 96 pounds of LH_2 could be burned. Therefore,

    TNT equivalent = (770 + 96) (0.65) (1.3)

    = 732 pounds
3. From the table, the safe distance is 750 feet.
4. From the equation, the *extreme* distance at which glass breakage may occur is:

    $d = (410) (732)^{1/3} = 3,740$ feet

It should be noted that the foregoing rules cannot be applied with absolute rigidity. Every proposal must be considered on its own merits. Thus, the severe limitations of the table can be ignored if there is reasonable evidence that a proposed design will prevent mixing of hydrogen with oxidizer. One possible approach is to enclose the hydrogen vessel and lines in ductwork, etc., inerted by nitrogen or carbon dioxide, and arranged so as to carry off a spill and mix it safely with air. Fast and positive means of shutting off flow are also valuable, if they can be devised.

In many cases, a better approach is to shield and contain the oxidizer tank, particularly if it contains oxygen; we cannot yet count on containing fluorine even under the best of conditions.

"Battleship" construction will naturally be considered superior to fly-weight construction.

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Pentaborane

INTRODUCTION

The mushrooming chemical technology of the past twenty years has provided a new and logical element, boron, on which to base fuels for rocket motors and air-breathing engines. Boron and certain boron compounds, as a fuel or a fuel additive, can provide up to 75 percent increase in the energy level per unit weight over the conventional hydrocarbons now in extensive use.

Boron, moreover, is available domestically from large and concentrated deposits of boron compounds and exhibits properties that appear desirable from a chemical processing point of view.

Boron combines metathetically with hydrogen to form more or less stable liquid compounds, known as the boron hydrides or, the boranes. The boranes occur in gaseous, liquid, or solid states; from the light diborane (B_2H_6, usually a gas), to pentaborane (B_5H_9, a liquid), to decaborane ($B_{10}H_{14}$, a solid). They are also quite chemically reactive in comparison to hydrocarbons. Boron-hydrogen molecules may be modified by adding certain hydrocarbon groupings, thus providing fuels (such as the alkyl boranes) with specific desired thermal properties. In addition, metal borohydrides are beginning to attract interest.

Of the six best known boranes, pentaborane is the optimum choice as a liquid rocket fuel. Its energy level of 29,100 Btu's per pound is far below hydrogen's ideal 51,000 Btu's per pound, but compares favorably to fuel oil and gasoline's 17–21,000 Btu's per pound. In addition, pentaborane has a wider range of flammability than hydrocarbons and will thus permit air breathing engines to operate at higher altitudes than are possible with conventional fuels.

Inherent in the utilization of most of the high energy propellants are problems of handling and storage. Boron hydrides are extremely chemically reactive and are quite sensitive to air and moisture. In addition, the boranes are highly toxic. Pentaborane, for example, is a volatile liquid the vapors of which will ravage an unsuspecting victim's

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nervous system. As a result, pentaborane requires special handling and storage, and extra design effort is necessary to remove the prod-·ucts of combustion as they are generated.

Uses for purposes other than energy sources are becoming quite feasible. For example, various boron compounds are already finding their way into domestic use as automotive fuel additives. Special industrial applications may also see boron hydrides utilized as reducing agents, antioxidants, and precursors of high temperature polymers.

SOURCE AND PREPARATION

Boron is an acid forming element. The properties of boron and boron compounds strongly resemble those of silicon and silicon compounds, although the two differ somewhat in molecular structure. In nature, boron occurs chiefly in boric acid and the salts of various condensed boric acids such as borax. Boron constitutes .001 percent of the earth's crust; in the Western United States it occurs in large deposits of certain minerals and brines.

Pentaborane occurs in small amounts of the crude gas resulting from the decomposition of magnesium boride. It occurs in two forms: B_5H_9 and B_5H_{11}. The latter is quite unstable, decomposing at room temperatures. A more practical way to produce pentaborane involves first the generation of diborane. Diborane, B_2H_6, is the simplest hydride of boron and the easiest to prepare in pure form. Three methods are possible in the preparation of diborane, but the method employing the reaction of boron halide with an electropositive metal is most often used to prepare diborane in large quantities. Pentaborane is formed by the pyrolysis of diborane at a temperature of 480° F, in the presence of excess hydrogen.

NATURE OF THE HAZARD

Pentaborane is a boron hydride existing at normal temperatures and pressures in the pure state as a clear, water-white mobile liquid with a characteristic pungent and nauseating odor. It is insensitive to mechanical shock and is considered stable at ambient temperatures under the blanket of an inert atmosphere.

Pentaborane is an extremely hazardous propellant due to its toxicity, high reactivity, and erratic pyrophoric or spontaneous ignition characteristics. Of these hazardous properties, toxicity is the most serious because of its deleterious effects on the central nervous system.

A liquid at normal atmospheric conditions, pentaborane must be stored under a dry, inert gas blanket. Extended storage can be accomplished reliably in small quantities in cool, well-ventilated areas at a safe distance from fire hazards.

PHYSICAL PROPERTIES

Pentaborane has two forms: B_5H_9, and B_5H_{11}. Both are colorless, mobile liquids. B_5H_9 has an extremely disagreeable odor; it decomposes over a long period of time to form hydrogen and a solid, colorless, nonvolatile hydride. B_9H_{11} also dissociates at room temperature, but within 24 hours, to form hydrogen, and certain solid clear deposits on the container walls. The physical properties that follow pertain to B_5H_9, the more stable, usable form of pentaborane:

Molecular Weight	63.17
Color	Colorless
Odor	Sour milk
Freezing (melting point), °F	−59.8
Boiling Point, °F	137.1
Specific Gravity, at 68° F	0.627
Density at 68° F, lb/ft³	39.14
Density at 68° F, lb/gal	5.23
Critical Temperature, °F	435.2
Vapor Pressure at 40° F, psia	1.6
Vapor Pressure at 60° F, psia	2.7
Vapor Pressure at 76° F, psia	4.0
Heat of Fusion, Btu/lb	92
Heat of Vaporization, Btu/lb	219
Heat of Formation, Liquid at 77° F, Btu/lb mol	13,904
Heat Capacity at 77° F, Btu/lb °F	0.57
Viscosity at 68° F, lb/ft sec	2.13×10^{-4}

CHEMICAL PROPERTIES

Pentaborane is soluble without reaction in inert hydrocarbon solvents such as toluene, kerosene, benzene, pentane, hexane, and No. 2 fuel oil. Other solvents, especially those containing reactive carbonyl groups and highly halogenated or highly oxygenated solvents, must not be employed for use in pentaborane since they can form shock-sensitive solutions. *Solvents of this nature, which definitely must not be used, are acetone, carbon tetrachloride and other ketones, and aldehydes.*

Pentaborane is a very reactive fuel. While in the pure state, it is insensitive to mechanical shock and exhibits satisfactory thermal stability at ambient temperatures in an inert atmosphere. Its autoignition temperature in air has been established at about 77° F.

In oxidation-reduction reactions, pentaborane behaves as a very strong reducing agent. It is hypergolic (self-igniting) with high-energy oxidizers such as chlorine trifluoride at atmospheric pressures, but an external ignition source is required to react pentaborane with hydrazine.

Several pentaborane reactions are of considerable importance in the handling of the propellant since they constitute the basis for propellant neutralization, disposal, and decontamination operations. Some of the typical reactions are:

1. Reaction with water (hydrolysis). Pentaborane reacts very slowly with water to yield boric acid and hydrogen gas. The delay of this reaction is due in part to the immiscibility (unwillingness to mix) of the reactants. The reaction takes place as follows:

$$B_5H_9 + 15H_2O \rightarrow 5H_3BO_3 + 12H_2$$
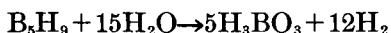
2. Reaction with alcohols. The reaction of pentaborane with alcohols is similar to that with water except that the reaction with alcohols is faster. The reaction of pentaborane with methanol and ethanol is shown in the following equations, respectively:

$$B_5H_9 + 15CH_3OH \rightarrow 5B(OCH_3)_3 + 12H_2$$

$$B_5H_9 + 15C_2H_5OH \rightarrow 5B(OC_2H_5)_3 + 12H_2$$
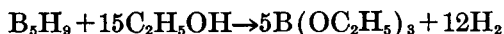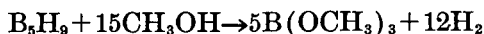
3. Reaction with ammonia. Pentaborane reacts with ammonia to form a salt-like compound which is stable at room temperature. The reaction takes place as follows:

$$B_5H_9 + 4NH_3 \rightarrow B_5H_9 \cdot 4NH_3$$
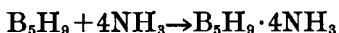
4. Reaction with oxygen (oxidation). Pentaborane vapors will ignite with pure oxygen. The reaction, whether explosive or normal, yields boron oxide and water as reaction products. The stoichiometric reaction is:

$$2B_5H_9 + 12O_2 \rightarrow 5B_2O_3 + 9H_2O$$
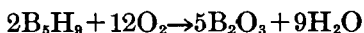
TOXICITY

Pentaborane is extremely toxic in both the vapor and liquid states. Exposure to pentaborane should be avoided by every possible means. The American Conference of Governmental Industrial Hygienists tentatively adopted, at their 1960 meeting, a Threshold Limit Value (TLV) of 0.005 ppm for an eight-hour day continuous exposure.

Pentaborane is toxic by skin contact, ingestion, or inhalation; symptoms occurring most frequently, however, are similar to intoxication, which may be attributed to inhalation. The median detectable concentration by odor has been reported to be from about 1 ppm to about 3 ppm. *It should be clearly understood that pentaborane concentrations which are detectable by odor are immediately dangerous.*

Physiological Effects

Symptoms of pentaborane exposure are dependent upon the vapor concentration, the individual, and the duration of the exposures. Since pentaborane reacts slowly with water, it tends to concentrate in fats and lipides and consequently exerts its toxic properties against the central nervous system. Typical symptoms of exposure to dangerous concentrations of pentaborane are nervousness, dizziness, lack of equilibrium, nausea, and frontal headaches. Temporary impairment of higher mental functions, lack of coordination, and transient amnesia for recent events are common.

Most frequently, intoxication cases occur from exposure to low concentrations of pentaborane over long periods of time. The symptoms of such exposure are similar to those resulting from lack of sleep, alcoholic hangover, and general physical exhaustion. The exposed individual may show indifference to his assigned tasks and lack of manual dexterity. Personnel suspected of being exposed to pentaborane should be placed in the care of a physician as soon as possible.

DYNAMIC HANDLING

Pentaborane is not only a high-energy toxic fuel but is also pyrophoric and can therefore react explosively with air. Although the propellant is insensitive to mechanical shock and moderate external heat under an inert atmosphere, whenever a pentaborane leak is experienced, the poison, fire, and explosion hazards become definitely prominent.

It has been shown that pentaborane can form shock-sensitive mixtures with many solvents usually found in propellant handling areas. In addition, there are certain materials and compounds that must not be used with pentaborane because of its highly reactive combination possibilities, its miscibility with various lubricants, and its extremely low viscosity and surface tension properties.

Emphasis on design factors and personnel training should contribute to the prevention of leaks and spills.

MATERIALS AND DESIGN

System Integrity

The hazardous properties of pentaborane allow no compromises in system integrity. The system must be extremely reliable, flexible, and easy to operate and maintain. Some of the design criteria for the system are as follows:

1. Only materials of construction which are definitely known to be compatible with pentaborane can be employed.

2. The number of mechanical joints must be minimized to reduce the probability of propellant leakage.
3. The propellant transfer lines must be free of liquid traps.
4. An inert-gas system must be provided to prepurge the propellant transfer lines.
5. An inert-solvent purge system must be provided also to remove the residual pentaborane in the transfer lines.
6. Provisions must be made to operate the system remotely.
7. The system vents should be ducted together and connected to a vapor scrubber, a high vent stack, or a flare stack, and must be provided with facilities to prevent air and water vapor seepage during shutdown periods.
8. Sufficient control equipment must be provided in order to isolate portions of the system during emergencies or component replacement operations.
9. The system vents must be provided with a flame arrester and a low-capacity inert-gas purge.
10. A pentaborane vapor monitoring device is mandatory.

The continuous automatic observation of an operational system for possible malfunctions can prevent serious propellant spills. Since small pentaborane leaks cannot be detected by odor or color, all joints in the system must be checked periodically with a commercially available sensitive pentaborane detector. This technique is practical since small propellant leaks yield high local vapor concentrations. Whenever a small leak is detected, corrective action must be taken as soon as possible.

Compatibility

Pentaborane is compatible with a wide spectrum of materials of construction. However, considerable care must be exercised in selecting suitable materials because of the hazardous properties of pentaborane and the ability of the propellant to react explosively with some materials. In addition, the safe handling of pentaborane depends largely on avoiding propellant leaks and spills, which in turn are dependent on the proper selection of compatible materials.

Pentaborane reacts with water, air, metal oxides, and organic compounds containing a reducible functional group. Consequently, the pentaborane storage and transfer systems must be free of air, moisture, rust, and contamination. The lubricants, solvents, and gaskets utilized in these systems must be chemically inert to pentaborane.

The hazards associated with the decontamination of pentaborane systems and components are significantly reduced when impermeable materials of construction are utilized. High porosity castings and gaskets should be avoided.

Compatible Materials

. The following lubricants and materials of construction have been found to be compatible with pentaborane:

Stainless Steel Type 302	Cadmium Plated Steel
Stainless Steel Type 304	Brass
Stainless Steel Type 321	Copper
Stainless Steel Type 347	Glass
Aluminum Alloy Number 6061–T6	Pure Carbons
Aluminum Alloy Number 7075–T6	Teflon
Alluminum Alloy Number 2024–T3	Kel-F Number 5500
Aluminum Alloy Number 3003–H14	Viton
Aluminum Alloy Number 356–T6	Viton A
Aluminum Alloy Number 5052–S	Graphitar Number 39
Aluminum, Cadmium Coated	Kel–F and Glass Yarn
Aluminum, Chromated	Fluoroflex T
Titanium Alloy, Rem-Cru No. C–110M	Fluorosilicon Rubber
Titanium Alloy, Rem-Cru No. C–130AM	Molybdenum Disulfide
Magnesium Alloy, Fed. Q.Q., M56, Comp. AZ63	Graphite Impregnated
Hastelloy No. X–1258	Asbestor
Monel, Soft, M–8330–B	Hercules No. 571 Kaobestos
Nichrome "v"	Rockwell Nordstrom Lube No.
Magnesium Alloy, Fed. Q.Q., M–44, Comp. A.	921

Materials such as low-carbon steel, iron, and neoprene are usually considered satisfactory for limited service in pentaborane. But, since these materials can be attacked by pentaborane, their use is definitely not recommended.

Certain materials and lubricants such as natural rubber, nylon, mylar, etc., have been found to be incompatible with pentaborane and must not be used.

The following compounds can form shock sensitive mixtures with pentaborane and must not be used:

Carbon Tetrachloride	Freons
Acetone	Chloroform
Trichloroethylene	Methylene Chloride
Thiokol Rubbers	Aldol
Methylvinyl Ketone	Alkyl Chloride
Ammonium Chlorate	2-(Chloromethyl) Ether
Acetyl Acetone	3-Chloropropene
Crotonaldehyde	1,4-Dibromoethane
Dioxane	1,2-Chloroethane
Ethylacetate	Methylene Bromide
Dimethyl Ether	Methylene Iodide
Acrolein	Trichloroethane
Ansul Ethers	Boron Trichloride
Acetaldazine	

Preparation of Materials

All components of a pentaborane transfer and/or storage system, must be properly prepared prior to installation. Preparation procedures consist of rendering the components chemically inert to pentaborane.

The preparation of materials generally consists of degreasing, descaling, passivating, and drying. The cleaning solutions can be applied by immersing, spraying, wiping, circulation, or any other manner as long as the surfaces to be cleaned are completely wet in the solutions. Any component which can trap or retain liquids should be drained or emptied between applications of different cleaning solutions.

Passivation

The passivation procedure for components fabricated of stainless steel is as follows:

1. Immerse for a minimum period of 30 minutes, at room temperature, in an aqueous solution containing from 45 to 55 percent (by weight) technical grade nitric acid.
2. Rinse with water to remove all traces of the passivating solution.
3. Dry by purging with dry, hydrocarbon-free, filtered nitrogen gas or by heating in an oven at 140° to 160° F.

> NOTE.—Acid passivation of components having highly polished or lapped surfaces may be omitted if the finished surfaces cannot be conveniently protected from the acid solution.

Components fabricated of aluminum or aluminum alloys can be passivated as follows:

1. Immerse for a minimum period of one hour, at room temperature, in an aqueous solution containing about 45 percent (by weight) technical grade nitric acid.
2. Rinse thoroughly with water to remove all traces of nitric acid.
3. Dry by purging with dry, hydrocarbon-free, filtered nitrogen gas or by heating in an oven at 140° to 160° F.

HANDLING

Facility Safety Equipment

Facility safety equipment should consist of personnel emergency showers, eye baths, a water deluge system preferably of the fog type, fire blankets, portable fire extinguishers, fire hoses, a pentaborane detector, first-aid kits, personnel shower facility, protective clothing and gas masks. This safety equipment should be strategically located and easily accessible.

A pentaborane detector such as is described in "Hand-operated Pentaborane Detector" (see bibliography) should be portable to facilitate the monitoring of the area for hazardous pentaborane concentrations, checking the system joints for leaks, determining when replaced components are properly decontaminated, and monitoring the water in the collection basin for hazardous pentaborane concentrations. To accomplish the above functions effectively, the detector should be extremely sensitive.

Personal Safety Equipment

All personnel in both local and remote handling and storage areas should wear fully protective impervious and flameproof clothing at all times.

HAZARD CONTROL

Due to the pyrophoric nature of pentaborane the only effective means of preventing fires is by preventing propellant leaks and spills. The time between the inception of the hazardous situation and initiation of control action must be reduced to a minimum.

Spill Control

The disposition of the spilled propellant should not be too difficult, especially if propellant handling is performed only during satisfactory weather conditions, and if steps are taken to isolate and dispose of spilled propellants immediately. The disposition method depends greatly on several factors such as the quantity spilled, prevailing weather conditions, and the location of storage and/or handling area, etc. The discussion presented herein, will be limited to general criteria applicable to most situations.

Spilled pentaborane can be disposed of effectively by setting it afire. (Sometimes this may not be required since pentaborane is pyrophoric at temperatures of about 77° F, or higher.) Setting the spilled propellant afire can be facilitated by the installation of a reliable ignition device in the drainage system between the storage area and the collection basin. In some cases, however, the amount of spilled propellant may be so small that the resulting water-pentaborane mixture is not ignitable. In this case, the propellant can be allowed to react with the excess decontamination chemicals in the collection basin. This operation must be monitored closely since pentaborane and water are not miscible; sufficient pentaborane may float on the water to cause a potential toxic hazard.

The storage area must be decontaminated thoroughly following a pentaborane spill or fire.

Fire Prevention and Control

To prevent fires, leaks and spills must be prevented. Pentaborane fires are controlled only from the point of view of preventing facility damage. As previously discussed, it may be advantageous to set spilled pentaborane afire as a means of hazard reduction.

STORAGE AND USE

Storage

Pentaborane can be stored for periods of at least three years without adverse effects to the container or propellant. Good results for extended storage can be obtained only by the use of clean, moisture-free vessels under an inert atmosphere. Excluding moisture prevents the loss of pentaborane through hydrolysis with the resultant formation of solid products which not only contaminate the propellant but also affect the operation of control equipment (valves, pumps, flow-meters, etc.).

The shipping containers in which the pentaborane is received are satisfactory for storage. Tank-farm storage vessels can be used if they are made of compatible materials, serviced properly, and if the propellant is maintained under an inert atmosphere.

Pentaborane shipping cylinders which have been opened must be monitored periodically for pressure buildup. This is necessary since pentaborane can react with water vapor and other contaminants liberating large quantities of hydrogen gas.

Transfer of Pentaborane

Pentaborane can be transferred by means of inert gas pressurization or a transfer pump. Gas pressurization unloading is used almost exclusively at the present time since this technique is extremely reliable. The transfer pump technique can be used also, but in this case a leak-proof pump is required.

TRANSPORTATION

Shipment of pentaborane by rail, water and highway carrier is authorized by the Interstate Commerce Commission (ICC). The propellant is classified by the ICC as a "Flammable Liquid," and is subject to regulations established for this group. In transit a flammable liquid label (RED) must be affixed to the cylinder as specified in the regulations. Highway carriers containing pentaborane must be identified with "Dangerous" placards in letters at least 3 inches high on a contrasting background. Rail express shipment of pentaborane is prohibited. Various quantities of pentaborane may be shipped, but the largest container presently authorized is limited to 1,000-lb water capacity.

RESEARCH NOTES

NASA's Lewis Research Center at Cleveland, Ohio, is the agency responsible to the space program in the important areas of power-plants and propulsion, high energy propellants, nuclear rockets, electric propulsion, and for such launch boosters as the Centaur.

Although research into high-energy propellants has been carried out for several years by various DOD Agencies and civilian firms, the laboratories at Lewis have rapidly gained a widely respected reputation in this realm during the relatively few years spent at this task.

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   The instrument described in this paper is a hand-operated monitoring device for the boranes employing a colorimetric reagent sensitive to these compounds and is capable of detecting 0.5 parts per million of pentaborane. The pentaborane monitoring device is essentially an MSA Samplair Pump. Filter paper is mechanically secured to the entrance of the pump. Operation of the instrument draws air through the reagent laden filter paper. The reagent consists of triphenyltetrazalium (TTC) chloride in solution with quinoline, pyridine and water and is prepared by placing 0.5 triphenyltetrazalium in a 50 m brown bottle, adding 2.5 ml water and 2.5 ml pyridine, and swirling until the TTC is dissolved. Twenty-five ml quinoline are then added and the bottle is capped and shaken until the solution is well mixed. If the reagent is kept from light and heat, it will keep indefinitely. A change to pink indicates presence of borons. A calibration chart is given in the article.

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The high reactivity of the boron hydrides made them potentially useful as ignition or relight fuels. Spontaneous ignition temperatures and ignition delays were determined for pentaborane in a hot-air stream. Ignition temperatures from 600° to 675° F were found for ignition delays of about 3 to 20 milliseconds over a range of pressure from 5 to 29 inches of mercury absolute. The effect of temperature on ignition is represented by the Arrhenius equation. The effect of pressure on ignition temperature can be represented by an equation of the type

$$p^n = K E^{-E/RT}$$

where p is absolute pressure, n and K are constants, E is the chemical activation energy, R is the universal gas constant, and T is absolute temperature. The apparent activation energy for the ignition of pentaborane in air increased from 21.8 to 31.6 kilocalories per mole as the pressure increased from 10 to 29 inches of mercury.

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An investigation of the spontaneous ignition limits of pentaborane-air mixtures was made at 25° C for pressures ranging from 0.3 to 75 centimeters. Mixtures outside the flammability limit may be prepared by slowly evaporating pentaborane into air or perhaps by spraying pentaborane into air. When air was introduced on or below the surface of liquid pentaborane at 25° C or less, any explosions that occurred were in the vapor-air mixture above the liquid.

The lower limit of spontaneous ignition was approximately 14 volume percent at 1 atmosphere and 55 volume percent at 0.1 atmosphere. The rich limit was not determined but mixtures containing 75 percent pentaborane ignited at 5 centimeters of mercury.

It is suggested that liquid pentaborane is less reactive than the vapor in contact with air at 25° C and below. Ignition and burning in these experiments always took place well above the liquid and the temperature of the liquid remained fairly close to room temperature.

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Liquid Fluorine

INTRODUCTION

Fluorine is chemically the most reactive of all the elements. It combines rapidly with most others, even with the noble gases, under extreme artificial conditions. It reacts with gold and platinum, but rather slowly. Fluorine decomposes water, attacks glass, and combines so vigorously with such random substances as cork, alcohol, and turpentine that they are set afire. It is these qualities that have built up an enormous psychological barrier against its usage.

Most fluorine compounds, however, are quite stable and have been used in refrigerants, aerosol propellants, and fluorocarbon resins. The few very reactive fluorine compounds have been used as reactive intermediates for unusual commercial-scale organic syntheses.

In the early days of rocketry, fluorine was considered as an oxidizer in liquid-fuel systems. Yet psychological resistance prompted researchers to work with reactive fluorine compounds (see chlorine trifluoride) as the next best thing. It is of interest to note that fluorine subsequently presented handling problems not significantly different from those of other highly reactive or toxic materials.

Preparation of fluorine for limited industrial usage has been underway for over 20 years; NACA and NASA have studied fluorine handling for bulk use as a rocket fuel oxidizer for more than ten years at the Lewis Research Center in Cleveland.

NASA's interest in any oxidizer better than the liquid oxygen that it has been using so successfully in the Thor, Atlas, and Saturn launch boosters would depend on a substantial improvement. It has been found that "spiking" liquid oxygen with 30 percent fluorine—"floxing"—increases payload from 10 to 30 percent. The fluorine-oxygen system is more tractable in present boosters than a pure fluorine system, and the F-O system is more feasible with certain modifications.

Several commercial companies have acquired first-hand chemical knowledge of fluorine by virtue of long years in production and shipping of the liquid and gaseous material. NASA's Lewis Laboratories,

with their vast hardware and handling research, have brought fluorine up to the level of quantity utilization. The Nation's space program is beginning to reap the benefits of their study of liquid fluorine's high potential as an oxidizer; it remains for industrial users to realize its potential in other fields.

SOURCE AND PREPARATION

The preparation of fluorine is not as complex and does not require as elaborate chemical apparatus as that necessary for many of the high energy fuels such as pentaborane. Rather, pure fluorine is prepared by methods similar to those used to produce other halogen elements. The most used process so far is the electrolysis process, but other methods are being studied.

Electrolysis involves passing a current through a solution of anhydrous hydrogen fluoride in fused potassium difluoride, with a composition of 40 percent hydrogen fluoride. Both hydrogen and fluorine gases are liberated, collected, and compressed to 2.5 psig; the fluorine is purified to 98.5 percent in an absorption apparatus and prepared for liquefaction. Fluorine is liquified simply by running it through a heat exchanger where heat transfer with a cryogenic liquid cools it into a condensate that is then tapped and sent to a storage area.

Fluorine is eighteenth in order of abundance of the elements in the earth's crust. Since fluorine forms ions so readily, and since most of its compounds are soluble in water, it is found in considerable quantities in minerals and in trace amounts in sea water; it is never found in the free state in nature. In the earth's crust, fluorine is most abundant in minerals: fluorite (or fluorspar-calcium fluoride), cryolite (a fluoride of sodium and aluminum), and fluorapatite (or phosphate rock—calcium fluoride combined with calcium phosphate). Phosphate rock reserves provide a vast supply for future consumption; presently fluorspar is the chief ingredient in the manufacture of the hydrogen fluoride for later use in the preparation of fluorine.

NATURE OF THE HAZARD

Fluorine is a greenish-yellow gas in the absence of moisture. A fluorine cloud released into the atmosphere generally has a reddish-brown appearance which changes to milky white when it reacts with the water in the atmosphere to form hydrogen fluoride. Fluorine condenses at $-306.5°$ F exhibiting a slight green fluorescence, giving it the yellowish-green appearance. At $-368.3°$ F fluorine solidifies to a yellow solid and at $-377.7°$ F the crystalline structure changes to produce a white solid.

Fluorine has a pungent odor characteristic of the halogens. However, the high reactivity of the material causes hydrogen fluoride to

be formed long before the material reaches the olfactory organs; consequently a faint odor similar to ozone is sometimes present.

The hazardous nature of fluorine is characterized by two properties: its chemical reactivity and its toxicity.

PHYSICAL PROPERTIES

Gas

Molecular Weight	38. 00
Oxidation Potential, Volts	−2. 85
Cp/Cv, 77° F and 1 atm	1. 36
Cp at 32° F, Btu/lb mole ° R	7. 5183
Cv at 32° F, Btu/lb mole ° R	5. 535
Critical Temperature, ° C, ° F	−129, −200. 5
Critical Pressure	55 atm. (808 psia)

Liquid

Density, −306.2° F g/cc	1. 51
Density, −320.4° F g/cc	1. 56
Boiling Point, ° F	−306. 5
Freezing Point, ° F	−363. 3
Vapor Pressure at 320.4° F. psia	5. 2
Vapor Pressure at Critical Pressure, psia	808. 5

Solid

Density, −335.4° F, gm/cc	1. 3 (81. 16 lb/ft^3)
Melting Point ° F	−365. 3
Heat of Fusion, −363.3° F, Btu/lb mole	219. 56
Transition Temperature, ° F	−377. 7
Heat of Transition, Btu/lb mole	313

CHEMICAL PROPERTIES

Chemical reactivity takes the form of either fire or explosion. Although the material is not shock sensitive and is non-flammable, it easily ignites organics, solvents, lubricants, etc. The greatest hazard of fluorine lies in its extreme reactivity and readiness to cause combustion of materials with which it may come in contact, thus yielding violent explosions.

Whether or not a substance will ignite spontaneously depends upon the following conditions of exposure:

1. Temperature and pressure of the system, if they approach critical valves.
2. Thermal conductivity of the substance if it is a solid.
3. Particle size or surface area exposed with respect to the mass of substance exposed.
4. Kinetic or static exposure.

Most organic materials react spontaneously with fluorine. Inhibition to reaction has been observed when the material is chemically

pure and exposure conditions are ideal. (One or two grams of petro-leum jelly placed on a warm, smooth surface resisted reaction when fluoride gas was impinged on the surface. However, simply by disturbing the smooth surface, instantaneous ignition was obtained.)

NASA has found that pressure increase will initiate reaction with fluorine. (A group of non metallic materials was tested under static conditions for compatibility with fluorine at atmospheric pressure and 1,500 psig. When a reaction did not occur at the lower pressure, experimentation showed that the reaction could be initiated by a pressure increase.)

Fluorine will react initially with the surface of nearly all solid materials. In the case of most metals the surface reaction simply forms a passive fluoride film (passivation). If the surface area is very large in proportion to its mass, (sheet) surface reaction will initiate combustion; the material reacts because the rate of heat dissipation is reduced. Most metals with a high thermal conductivity will resist reaction with fluorine simply by dissipating the heat of reaction.

TOXICITY

The toxicity hazard is both chronic and acute, especially when the inhalation of fluorine or hydrogen-fluoride-contaminated air occurs over prolonged periods. With exposure of the tissue to high con-centrations of the gas, poisoning soon becomes apparent. Exposure to jets of liquid or gas causes immediate and deep burning of the skin.

The American Conference of Governmental Industrial Hygienists indicates the Threshold Limit Value for fluorine inhalation for men is 0.1 ppm (or 2 mg per cubic meter) per eight-hour working day. The threshold concentration for detecting fluorine by its odor is generally regarded to be three ppm. Anyone working with fluorine should leave the area within 15 minutes if fluorine odor is detected, and if the odor becomes pungent, the area should be evacuated immediately.

As stated previously, a jet of liquid fluorine striking the body will cause severe burns that are difficult to heal. The tissue destruction is the result of oxidation by the fluorine, thermal damage from heat, and tissue poisoning by the formation of hydrofluoric acid.

DYNAMIC HANDLING

MATERIALS AND DESIGN

With fluorine, the key to using compatible materials has not been so much the choice of metals as the cleanliness. On tests run by NASA, including the impinging of 350-feet-per-second streams of fluorine against samples, designers found no metal erosion. Upon review of the program, it was found that the failures that did occur in flourine

systems were due to system contamination, not to materials. Contaminants include all foreign materials, whether organic or inorganic.

A secondary cause of burnouts is the mechanical failure of the containing system which allows the fluorine to contact reactable materials. Permeability is one of the controlling factors in corrosion rate, and the fluoride coating varies with the material. The least reactive, or the most resistant metals, are the least dependent on the fluoride film. For this reason, metals are tested under the most severe condition; those investigated include nickel, Monel, Inconel, the 300 series stainless steels, brass, copper, and some aluminum alloys (much on the same order as will be noted in the Chlorine Trifluoride chapter).

All fluorine systems, either for static or flow conditions, must be dry and leakproof in addition to being fabricated of compatible materials which have been properly cleaned and passivated. The following materials have been satisfactorily used for fluorine system components:

Component	Gaseous Service	Liquid Service
Storage tanks	Stainless steel (304L, 347)	Monel.
	Aluminum 61	Stainless steel (304L, 347).
	Mild steel (low pressure)	Aluminum 61.
Lines, Fittings, and Flanges.	Stainless steel 300 series	Monel.
	Aluminum	Stainless steel 300 series.
	Copper	Aluminum 60.
	Brass	Inconel.
	Mild steel (low pressure)	Copper (low pressure).
Valve Bodies	Nickel	Nickel.
	Monel	Monel.
	Stainless steel 300 series	Stainless steel 300 series.
	Inconel	
	Brass	
	Bronze	
Valve seats	Nickel	Nickel.
	Copper	Copper.
	Brass	Aluminum.
	Aluminum	Brass.
Valve plugs	Monel	Monel.
	Stainless steel 300 series	Stainless steel 300 series.
Seals: Gaskets	Soft aluminum	Soft aluminum.
	Soft copper	Soft copper.
	Teflon	
	Kel-F	
O-ring	Aluminum, Teflon	Copper, aluminum or stainless steel (hollow-pressurized).
Chevron packing	Kel-F	
Washer packing	Lead	

Teflon

NASA has found that Teflon can be exposed statically to liquid fluorine at 1,500 psig without a reaction. However, it reacts with fluorine under flow conditions at 50 psig. Teflon does not form an inert film on exposure to fluorine; rather, it tends to break down and form low molecular weight fluorocarbon. These light fluorocarbons do not adhere to the surface and are of no use as a protective film.

Cleaning

Following the design and fabrication of a fluorine system from recommended materials, the next step is cleaning. First, the obvious dirt is removed by soap and water, steam cleaning, etc. Then comes a 10 to 20 percent nitric acid wash followed by distilled water rinsing. The rinsing is followed by drying, using an agent such as acetone, which in turn is purged by an inert gas. No contaminant can or should be overlooked. The system should then be assembled, purged and evacuated. Once the system is assembled, every effort should be made to avoid outside contamination. Pressurization with a dry inert gas to slightly (5 to 10 psig) above atmospheric pressure is helpful.

Passivation

The next step is the passivation of the system. Gaseous fluorine is introduced gradually, to about 50 psi and held for 8 hours. This allows time not only for fluorination of contaminants but also for build-up of the fluoride film.

Fabrication

In fabricating a fluorine system emphasis must be placed upon achieving a leakproof system and avoiding irregularities within the flow passages.

In tank fabrication a smooth, crevice-free interior must be achieved. Poor seam welds which have flux and slag inclusion, pockets, or bubbles are considered hazardous. To insure quality, all welds should be X-rayed.

Lines and fittings must be leakproof. The best way to join fluorine flow lines is to Heliarc (or inert weld) using a V-notch butt weld. For removable sections the use of concentrically serrated flanges with aluminum gaskets is advisable. Bolt tension should be checked, especially after extreme temperature cycling.

Fittings

Compression fittings and threaded connections have been successfully used on high pressure fluorine lines up to $3/4$ inch. Above $3/4$ inch they are not considered reliable, because large compression fittings are difficult to seat properly and tend to fail at high pressure.

Threaded connections should be avoided but have been used success-
fully when silver soldered, welded, or brazed. There are no thread
compounds completely inert to fluorine although fluorocarbon greases,
Molylube, litharge (lead monoxide) and glycerine, or Q seal, are most
commonly used successfully if care is taken to apply the material to
the last contacting threads in order to avoid contamination.

Most standard gas service valves, if constructed of compatible ma-
terial, can be used for gaseous fluorine service by using Teflon valve
stem packing. Liquid fluorine requires a diaphragm, or bellows seal
valve, because at the extremely low temperatures of a liquid fluorine
system the thermal shrinkage of Teflon packing is different from that
of the metal. However, valve bonnet extensions can be used to main-
tain a warm gas pocket for the packing. All hand operated valves
should be used only on low-pressure gas and even then should be
mounted with extension handles through a shield. Remotely operated
diaphragm or bellows seal valves should be used on high-pressure
liquid systems.

Any flexible tubing used in liquid fluorine work must be constructed
of compatible metal. Other than this requirement, the usual criteria
for a high-pressure flexible system holds.

Flow Metering

The commonly measured parameters in fluorine systems are flow
rate, pressure and temperature. Very reliable types of flow measure-
ment devices are orifices or rotameters for gases, and orifices or ven-
turies with differential pickups for the liquids. (Rotameters con-
structed of compatible materials have been used for a month of inter-
mittent service at NASA, but the hydrogen fluoride in the gas will
eventually etch the glass tube.)

Rotating vane flowmeters have been used successfully in liquid
fluorine operation. With proper care and cleaning they can be used to
pressures up to 1,200 psig.

STORAGE

Gaseous fluorine must be stored in cool, dry, well-ventilated sheds
well away from other fuels and oxidizers. Storage vessels holding
fluorine under pressure should not be exposed to fire, direct heat, or
sunlight. Nor should they be stored near steam lines. They should
never be approached until it is established that all valves are closed
and there are no leaks.

Liquid fluorine must be stored in a tank that is completely immersed
in liquid nitrogen. The storage vessel must be fitted with an alarm
system that will indicate a build-up of fluorine gas pressure or dan-
gerously low liquid nitrogen level.

Barricades

Barricade systems should be used. They will vary depending on the building, its construction and geographical location, the type of ventilation, the amount of fluorine being handled, etc. A barricade will serve to deflect a jet of fluorine and resulting molten metal globules which would issue from a broken high pressure gaseous or liquid fluorine system component.

DYNAMIC HANDLING

Personnel

The nature of the material dictates the need for safety equipment for personnel. The facility itself should contain emergency showers, eye-wash fountains, a fog type water system, portable fire extinguishers, and first aid kits.

Liquid fluorine always should be handled remotely. Persons necessarily involved in transfer work wear protective personal equipment. Face shields are worn whenever personnel approach equipment containing fluorine. Face shields offer limited protection against air-diluted blasts of gaseous fluorine. Clean impermeable gloves are worn when directly handling equipment which contains or has contained gaseous fluorine, to afford protection not only against fluorine but also against films of hydrofluoric acid which may be formed by escaping fluorine reacting with moisture in the air. Safety glasses are worn and metal frames are preferred to plastic frames.

Transferring

Liquid fluorine is easily transferred by pressurization with helium. Most important to this operation is the purity of the helium, which should be clean and dry. Purity can be assured by placing several filters plus a liquid nitrogen moisture and oil trap in the helium gas flow line. Filters and oil traps should be cleaned frequently to avoid build-up of contaminants.

Disposal

In nearly all fluorine operations very small quantities of the material can be safely vented to the atmosphere. If a large quantity is to be disposed of, direct venting is inadvisable. NASA has found that the reaction of fluorine with charcoal will produce mostly inert CF_4 gas.

Other disposal methods include the burning of gaseous fluorine with a fuel followed by the disposal of hydrogen fluoride; the reaction of gaseous fluorine with caustic solution followed by the disposal of sodium fluoride with lime slurry; and the reaction of gaseous fluorine with chlorides to release chlorine which can be neutralized with a

caustic solution. The last method is suitable for the laboratory; the others can be utilized for high disposal rates.

Purging

Any equipment that has contained fluorine must be purged with a dry inert gas before disassembly. If the amount of fluorine to be purged is large, precautions must be taken in its disposal.

System Disturbances

Repeated bending or vibrating of fluorine piping or tankage should be avoided because such action might cause mechanical failure of the equipment or impair the integrity of the fluoride film.

HAZARD CONTROL

Because of the violent nature of a true fluorine fire, fire control must be base on minimizing damage. The supply of fluorine should be shut off immediately. If this is not possible, fire fighters should wait until the fluorine has reacted. Then the fire can be handled as an ordinary blaze. *The addition of water to fluorine could result in an explosion.* It must be remembered that during a fluorine fire large amounts of unreacted fluorine and hydrogen fluoride are in the immediate atmosphere. After the fire, hydrogen fluoride will still be present.

SHIPPING

The shipping of fluorine as a gas at 400 psig pressure calls for considerable effort and results in high costs. This method is inadequate to meet the demands of even medium scale studies. (It is interesting to note that NASA participated in the liquid fluorine trailer program. In 1955, an experimental trailer consisting of a 586-pound fluorine tank under complete immersion in a tank of liquid nitrogen was driven for a total of 82 hours on and around the grounds of NASA Lewis Laboratory in Cleveland, Ohio. See "Transportation of Liquid Fluorine" in the Bibliography.)

RESEARCH NOTES

The following information reflects more than 10 years of dynamic handling and usage of liquid fluorine by NASA's Lewis Laboratories.

In the field of chemical fuels and oxidizers, the state-of-the-art has just about reached a peak. It remains only for the development of handling procedures and hardware, which almost always trails behind, to be brought up to date to make such chemicals useful. Since the material in this section refers to the concurrent development of fluorine handling technology and the development of fluorine as an

oxidizer, it is felt that some abstracts may be useful to the potential fluorine user.

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    Nickel, monel, and aluminum are resistant to attack by gaseous fluorine up to 450° C, while the resistance of stainless steels is unsatisfactory above 200° to 250° C.

    The corrosion of 3S–0 (3003–0) and 52S–0 (5052–0) aluminum, AISI 347 and 321 stainless steels, "A" nickel, and low-leaded brass was determined from the weight change of specimens exposed alternately to liquid and gaseous fluorine. Experiments were continued for a total exposure time of up to 3½ months. It was found that corrosion is negligible under the conditions of the experiments. No visual differences were observed between those surfaces exposed to the gaseous phase only and those exposed to both the liquid and the gaseous phases.

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ORDIN, P. M., "Transportation of Liquid Fluorine," NASA-Lewis, NACA RM
    Describes a 500-gallon-capacity liquid fluorine tank, its design, and procedures for filling and transferring liquid fluorine.

    Over a three-day period 100 cylinders of gaseous fluorine were fed into the main tank. It was condensed to a liquid by means of an outer jacket consisting of 100 gallons of liquid nitrogen. The theoretical amount of liquid nitrogen required to condense one pound of fluorine from 298° K was 1.72 pounds. No difficulties were encountered during storage, transfer or in driving the tank around the area.

PRICE, H. G., Jr.; AND DOUGLASS, H. W., "Material Compatibility with Gaseous Fluorine," NACA RM E56K21, January, 1957.

    This report describes a qualitative investigation of various nonmetallic materials for use with fluorine. To use this very active oxidizer, special materials must be examined for application in the flow systems, for example, as seal materials, thread lubricants, and hydraulic fluids for instruments and other equipment. These tests eliminated many materials from further consideration for use in fluorine systems. Several materials were found compatible at atmospheric pressure. Only Teflon and ruby (aluminum oxide) were compatible under the static conditions of the tests at 1500 pounds per square inch gage. Further tests under dynamic conditions are required if the application involves exposure to flowing fluorine.

———— NASA-Lewis, "Nonmetallic Material Compatibility with Liquid Fluorine," NACA RM E57G18, 1957.

ROLLBUHLER, R. J.; KINNEY, G. R.; AND LEOPOLD, L. C., NASA-Lewis, "Field Experiments on Treatment of Fluorine Spills with Water or Soda Ash," NASA TN D–63, September, 1959.

    An investigation was made of the use of water or soda as a deluge agent in reducing contamination from accidental fluorine spills. Six tests were carried out in a structure which might be typical of a building in which fluorine is used. Three of the tests were with gaseous-fluorine releases, and three were with liquid-fluorine releases.

    In all the tests, 30 to 43 percent by weight of the released fluorine was captured by the deluge agent. When gaseous fluorine was released and sprayed with water, there were no visual indications of fast reactions, and there was no test-structure damage. However, the reactions were rapid enough to result in considerable amounts of fluorine being captured within a few minutes. When liquid fluorine was spilled, there were violent reactions whether the deluge agent was present or not. The resulting structural dam-

age caused rapid loss of fluorine, but the amounts captured in these tests were about the same as with gaseous fluorine in spite of the losses, indicating faster reaction with water for the liquid-fluorine tests.

RUFF, OTTO; AND BRETSCHNEIDER, OTTO, "Die Reaktionsprodukte der verschiedenen Kohlenstossformen mit Fluor II," *Zs. f. Anorganische und Allgemeine Chem.*, Bd. 217, pp. 1–18, Heft 1, 1934.

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SCHMIDT, H. W., NASA-Lewis, "Compatibility of Metals with Liquid Fluorine at High Pressures and Flow Velocities," NACA RM E58D11, July, 1958.

The results of this investigation showed that turbulence, fluid friction, and impact effects, resulting from high-pressure, high-velocity liquid-fluorine flow through clean tubing or past irregularly shaped or sharp-edged objects, are not likely to initiate fluorine-system failures. The successful operations achieved in this series of compatibility tests can be attributed to the meticulous care that was taken in the assembly, cleaning, and passivation techniques used before exposure of the system to severe dynamic fluorine service. Therefore, improper choice of hardware, poor assembly techniques, and inadequate cleaning and pickling procedures can be considered the primary causes of fluorine-system failures.

―――― NASA-Lewis, "Reaction of Fluorine with Carbon as a Means of Fluorine Disposal," NACA RM E57E02, 1957.

Use of liquid or gaseous fluorine often involves disposal of small quantities of excess or residual material remaining in the system. Large quantities of fluorine may also be released in the event of refrigeration failure or by leakage in liquid-fluorine storage or transport containers.

The high toxicity of fluorine makes direct venting to the atmosphere inadvisable in most locations. Therefore, a method for safe, controlled, and efficient fluorine disposal is desirable.

From this investigation it can be stated that wood charcoal provides an economical and easily controlled method for fluorine disposal.

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Chlorine Trifluoride

INTRODUCTION

Fluorine has long been recognized as one of the most powerful oxidizers of all known elements. In recent years extensive research and development work has been done and handling and storage procedures as well as necessary hardware for this highly reactive oxidizer have been improved to a utilitarian level. But before such hardware was developed, several related fluorine compounds were studied, as far back as the late 1940's and early 1950's, to overcome the seemingly insurmountable disadvantages of liquid fluorine. Some of the combinations of compounds considered were chlorine-fluorine, nitrogen-fluorine, and fluorine-oxygen. Thus, researchers were after substances which would utilize some of the attractive fluorine properties but pose fewer handling difficulties.

American interest in chlorine trifluoride dates back to the 1920's and 1930's when little more than basic preparation was done. German interest in it during World War II led on to industrial production. Following the war, interest in the use of chlorine trifluoride in organic synthesis work increased although the compound was subsequently considered too reactive. Chiefly of interest as a liquid rocket oxidizer, it came into its own in 1947 when commercial quantities became available.

Chlorine trifluoride resembles fluorine in its commercial properties, especially its extreme reactivity, although its reactivity in a chemical system is somewhat lower. Its greatest advantage over fluorine is its noncryogenic storability as evidenced by its high critical temperature and boiling point.

In the late 1940's and early 1950's NACA did considerable work on chlorine trifluoride propellant systems using a 100-pound thrust rocket motor. It was stated that throughout the investigation no serious difficulties were encountered in handling the propellant, even though the combination is hypergolic (self-igniting) with all fuels.

Later NACA compared the performance of hydrazine-nitrogen tetroxide and hydrazine-chlorine trifluoride in a 300-pound thrust rocket motor. Transfer of chlorine trifluoride was accomplished in the liquid phase.

Further related NASA work with chlorine trifluoride included its use as an ignition lead in various nonhypergolic fuel systems.

SOURCE AND PREPARATION

Classified as an interhalogen, chlorine trifluoride, ClF_3, may be produced by a one-step direct combination process:

$$Cl_2 + 3F_2 \text{ (excess } F_2) \rightarrow 2ClF_3$$

Streams of pure chlorine and fluorine are introduced into a nickel reactor tube packed with silver-plated copper chips and held. The end product is collected in a quartz trap at a temperature of $-94°$ F and further purified to remove the hydrogen impurities.

Originally chlorine trifluoride was produced in quantity in a two-step process. In this German development chlorine and fluorine were allowed to react, under heat, to form chlorine monofluoride. The second step brought chlorine monofluoride together with fluorine to produce chlorine trifluoride on a scale of 300 pounds per hour yielding 96–98 percent.

NATURE OF THE HAZARD

Solid chlorine trifluoride is white; liquid ClF_3 is pale green-yellow, and as a gas, it is colorless.

Chlorine trifluoride is a very strong oxidizer, reacting with most organic and inorganic materials. Under ordinary conditions it reacts violently with ice or water; at higher temperatures it will vigorously ignite most common metals.

PHYSICAL PROPERTIES

Molecular Weight	92. 46
Boiling Point, ° F	53. 15
Freezing Point, ° F	−105. 38
Specific Gravity at B.P	1. 85
Density, lb/ft³ at B.P	115. 46
Vapor Pressure, psia at 60° F	17. 2
Vapor Pressure, psia at 100° F	39. 7
Vapor Pressure, psia at 140° F	80. 6
Viscosity, lb_m/ft-sec at B.P	3.21×10^{-4}
Surface Tension, lb_f/t at B.P	0. 00170
Critical Temperature, ° F	307
Critical Pressure, psia	837. 7
Heat of Fusion, Btu/lb at −103.3° F	35. 4
Heat of Vaporization, Btu/lb at B.P	128. 1
Heat Capacity, Btu/lb ° F at 41.16° F	0. 308
Heat of Formation, K cal/gm. mole	−80.100
Heat of Formation, Btu/lb mole	−44. 5

CHEMICAL PROPERTIES

• Chemical reactivity takes the form of either fire or explosion. Although the material is insensitive to mechanical shock and is nonflammable in air, it easily ignites organics, solvents and lubricants in the same order as fluorine. It is especially reactive with moisture. The greatest hazard of the material lies in its extreme reactivity and readiness to cause combustion of materials with which it comes in contact, and in the violent explosions which may accompany the reaction. As a result, spills and leaks are extremely dangerous, and the areas of storage and use must be kept clean. The liquid is more chemically active than the gas.

TOXICITY

Chlorine trifluoride is a toxic chemical; inhalation of even dilute concentrations is dangerous. Exposure of the skin and eyes to either the liquid or the gas is also dangerous, because of the oxidizing nature of the material. Severe burns and ulceration can result.

A Threshold Limit Value of ClF_3 in air of 0.1 ppm was adopted by the American Conference of Governmental Industrial Hygienists. This value represents the average concentration to which most workers can be safely exposed (over a normal work day) for extended periods without ill effects.

The odor threshold for the vapors is very low but not very accurately known. It is true, however, that its halogen-pungent type odor can be detected at sufficiently low concentrations that exposed personnel may not experience adverse effects if they evacuate the area immediately.

Exposure to odorously detectable concentrations can cause gasping for breath, swelling of eyes and eyelids, cloudiness of the cornea, lachrymation (tears), severe salivation, coughing, breathing difficulty, and convulsions. Concentrations sufficient to be fatal would be so irritating to eyes, throat, and lungs as to be violently intolerable to anyone in the area. Concentrations of 50 ppm or more may be fatal in 15 to 30 minutes. Like pure fluorine, a jet of chlorine trifluoride striking the body will cause severe burns that are difficult to heal. The tissue destruction is the result of three factors: first, oxidation by the material itself; second, thermal damage from the heat of oxidation; and third, tissue poisoning as a result of hydrofluoric acid being formed.

The slightest contact with human tissue should be countered immediately by flushing with large amounts of water to remove the hydrogen fluoride that is formed by reaction with the skin.

DYNAMIC HANDLING

Cleanliness is the key to safety in all chlorine trifluoride operations. Although the material is extremely reactive, it can easily be contained within vessels fabricated of the so-called compact metals. Due to the formation of a passive metal fluoride film, such metals as Monel, copper, stainless steel, etc., will protect the container from further attack.

All systems, either for static or flow conditions, must be dry and leak-proof, fabricated of compatible materials, and properly cleaned and passivated.

MATERIALS AND DESIGN

The following materials, when properly cleaned and passivated, are compatible with chlorine-trifluoride.

Stainless Steels Type 302, 304, 316, 321, 347 (preferred)
Chromium-Plated Steel
Aluminum Alloy Numbers 356, 1100, 2024, 5052, 6061, 6063, 6066
Aluminum Alloy Tens 50
Copper
Nickel (preferred)
Monel (preferred)
K-Monel (preferred)
Nickel-Base Superalloy Rene 41
Indium
Boron Carbide
Nitralloy
Kentanium 162B
Teflon has been found to be compatible under static conditions.

Chlorine trifluoride attacks glass, asbestos, and occasionally ignites Teflon.

Carbon, lead, Kel-F, and carbon steels are usually considered satisfactory for limited service. Soft copper and Teflon impregnated with 40 percent calcium fluoride are acceptable gasket materials.

Passivating

After a chlorine-trifluoride system has been cleaned, dried, assembled and leak checked, the system must be passivated with a small amount of chlorine trifluoride or gaseous fluorine. If used properly, either oxidizer will react not only with the metal surfaces to form an unreactive film but also with any residual contaminating material.

Before passivating the system, it should first be evacuated for at least an hour to remove any volatile contaminants. The first oxidizer to be introduced should be low pressure, for example, 15 to 20 psig for about 5 minutes; the later higher pressure (up to 50 psig for

fluorine or vapor pressure for chlorine trifluoride). After reducing to
·ambient pressure, the system may be considered passivated.

STORAGE

The material may be stored safely for several years if placed in a
dry, cool area. The containers in which the material is received are
satisfactory although frequent inspections of valves and fittings are
necessary because of the possibility of corrosion. A slight leak, well
below the odor threshold in a properly ventilated area, may be evi-
denced by a hydroscopic, porous green deposit around the valve outlet,
or leak point.

HANDLING

Chlorine trifluoride can be discharged from a storage container by
any one of three methods: by pressurizing the container with dry
nitrogen or helium, by transfer pump unloading, or by pressure differ-
ential generated by its own vapor pressure. Gas pressurization is
currently used because it has been proved reliable; vapor pressure
unloading is often impractical.

A fourth method, although it is seemingly the safest, is potentially
the most dangerous. This method involves the transfer by vaporiza-
tion of the liquid in the storage container, actual transfer to the use
tank in the gas phase, and finally condensation in the use tank. The
method seems safest because a gas with low molecular concentration
as opposed to a liquid with high molecular concentration is being trans-
ferred. However, the method is extremely slow and there is the possi-
bility that chlorine trifluoride will condense in pools at low points in
the transfer line, clogging lines and endangering operation.

In all three recommended transfer procedures adequate venting
and flush lines must be installed between the storage vessel and the
use tank.

HAZARD CONTROL

Spills

The most effective means of preventing chlorine-trifluoride fires is
by preventing spills or leaks. The disposition of material should not
be too difficult if outdoor handling is accomplished only under satis-
factory weather conditions. Spills are best controlled by allowing
the propellant to vaporize. At first a large amount will flash, cooling
the remaining liquid, and a steady state boiling will follow.

If a spill is deluged with large quantities of water, the water will
react with the material to form hydrofluoric acid. Large amounts of
energy will be released. The method is not generally used because of:

1. The formation of hydrofluoric acid, an acid which etches glass,
   which must then be disposed of.

2. The possibility of explosion.
3. The rapid vaporization which could result in prohibitive vapor·
   concentrations.

Fires

Because of the intense heat of most chlorine-trifluoride fires, fire control consists of minimizing facility damage. The facility, like the storage area, must be fire resistant, easy to keep clean, and equipped with a fog-type water system.

Personnel

The nature of the material dictates the need for adequate safety equipment for personnel. The facility itself should contain emergency showers, eye wash fountains, a fog-type water system, portable fire extinguishers, fire hoses, a chlorine-trifluoride detector, and first-aid kits.

Personnel in the area should wear flameproof clothing at all times. All personnel actually performing propellant transfer operations should wear fully protective equipment. Even if the operation is performed remotely, as is preferable, at least two operating personnel should be present and fully protected. Personnel protective equipment, the same as that used for fluorine, is recommended.

This equipment must be kept clean and in good operating order. A contaminated suit can be a definite hazard.

DECONTAMINATION

The removal of a component from a chlorine trifluoride system is potentially hazardous because it must be assumed that the piece is contaminated. Decontamination involves the removal of chlorine trifluoride, hydrofluoric acid and other fluorides following a propellant spill, or fire, or the deactivation of equipment.

Before removing the piece from the system, the piece must be purged thoroughly with nitrogen gas. It must then be removed and washed in hot water and dried with nitrogen. All personnel in these operations must wear protective clothing.

SHIPPING

Shipment of the material by common carrier is authorized by the Interstate Commerce Commission which classified chlorine trifluoride as a "corrosive liquid." The material is conveniently available in 5, 10, 25, and 100 to 200 pound cylinders, all of which are equipped with two valves—one in the vapor phase, and one in the liquid phase.

RESEARCH NOTES

Major research delving into the properties and handling of chlorine trifluoride has been generated chiefly by commercial chemical industries and by various agencies and industries under DOD auspices. The material presented in the handling section is based mainly on firsthand experience by researchers at Temple University.

NASA's interest in chlorine trifluoride has been in its use as a propellant oxidizer, the handling and performance characteristics of which have been available for a few years.

Chlorine trifluoride handling is quite similar to fluorine handling. NASA has been studying these materials for several years and treats both materials as highly reactive compounds.

The following reports are evidence of NASA's interest in the use of chlorine trifluoride as a potential rocket oxidizer. These reports, in addition to the material in Chapter 3 about fluorine, may be helpful.

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GREGORY, J. W.: AND STRAIGHT, D. M., "Ignition of Hydrogen-Oxygen Rocket Combustor with Chlorine Trifluoride and Trimethylaluminum," NASA-Lewis, NASA TN D–684.

HARTRIDGE, H., AND ROUGHTON, F. J. W., "A Method of Measuring the Velocity of Very Rapid Chemical Reactions," Proc. Roy. Soc. (London) Ser. A, vol. CIV, no. A726, pp. 379, 1923.

ORDIN, P. M.; AND MILLER, R. O.: "Experimental Performance of Chlorine Trifluoride-Hydrazine Propellant Combination in 100-Pound Thrust Rocket Engine," NASA-Lewis, NACA RM E9F01, August, 1949.

"Research on Materials and Methods for Decontamination of Toxic Missile Propellant Spillage," Technical Documentary Report Number ASD–TDR–62–64.

After conducting a literature survey and setting up some experimental work with NH_4OH, $NaHCO_3$, Na_2CO_3, $Ca(OH)_2$, $CaCO_3$, and urea, the authors concluded that all the carbonates look promising. If the reactions proceeded as desired all the end products would be reduced to a tolerable level. The carbonates were applied in the form of dry powder, a water slurry, and a water solution. The hydroxides also showed promise. Again, if reactions proceeded as desired, the end products would be either non-toxic or reduced to a tolerable level. Organic compounds appeared to offer no advantage over the inorganic compounds studied. Large quantities of heat are evolved and the reaction products were found to be varied and unpredictable. Toxic chlorofluoro compounds could be generated. A water solution of urea, according to the authors, appeared to warrant some experimental work primarily because this type of compound seems to have some potential for decontaminating propel-

lants such as nitrogen tetroxide and UDMH (unsymmetrical dimethylhydrazine). It can be concluded that water slurries and dry powders are not nearly as effective decontaminants for chlorine trifluoride as the solutions. There is no advantage in using slurries or dry powders over using neat water. The authors claim that the addition of an alkaline material to water has little or no effect on fluorine pickup. It did have an appreciable effect of chlorine pickup, values as high as 86.5 percent chlorine recovery having been achieved. This compares to a maximum value of 21.1 percent for chlorine using neat water.

ROLLBUHLER, R. J.; AND TOMAZIC, W. A., NASA-Lewis; "Comparison of Hydrazine-Nitrogen Tetroxide and Hydrazine-Chlorine Trifluoride in Small-Scale Rocket Chambers," NASA TN D-131.

The Handling and Storage of Liquid Propellants, Office of the Director of Defense Research and Engineering, Washington, D.C., pp. 47 to 54, 1961.

In the event of fire involving chlorine trifluoride, recommendations for fire control include the use of a dry powder sodium carbonate base extinguishing agent. Application must be made judiciously to assure a steady and controlled reaction between the extinguishing agent and the ClF₃. Bulk application of either agent might give rise to violent explosions and splattering. Coverage of the area with a fine water spray or mist will help minimize the evolution of HF and HCl fumes since both are water soluble. The authors also note: A special powder type agent may also be used on fires supported by chlorine trifluoride. This powder is made by mixing 20 parts by weight free flowing powdered fluorspar and 30 parts by weight commercial sodium bicarbonate base commercial fire extinguishing agent. It must be expelled from a suitable pressurized container, using carbon dioxide or nitrogen as propelling agent at 200 p.s.i. However, the powder residue, after application to a chlorine trifluoride supported fire, will contain active chlorine trifluoride and must be disposed of either by burial or surface disposal in a remote area. Buildings or shelters must be provided to shade storage containers from the sun. Buildings should be the roofed, open shed type.

WEYMOUTH, R. R., "Hydrazine-Chlorine Trifluoride Combustion and Performance Calculations," Bell Aircraft Corporation, Report Number 56-982-008, Contract W33-038ac14169 (Project Rascal), 1947.

Ozone

INTRODUCTION*

Ozone is a highly active, allotropic form of oxygen. It has been known since 1785, the year in which van Marum observed the formation of this gas resulting from an electric spark discharged in oxygen. Schoenbein recognized ozone in 1840 as a new substance. It was not until 1866 that Soret showed that the chemical composition of ozone is the same as that of triatomic oxygen.

The term ozone is derived from the Greek "ozein" meaning "to smell." Its pungent odor is sensed soon after an intense, nearby bolt of lightning during a storm; a concentration of under one ppm is all that is necessary to detect its presence.

As a liquid, ozone was known as far back as 1880, but only in recent years has it been prepared. There are many commercial applications for gaseous ozone; for example, in purifying drinking water, preserving food (cold storage) and bleaching, as well as in producing waxes, oils, textiles, bactericides, and peroxide.

As a potential rocket oxidizer, ozone is as extreme in its energy potential (it ranks with fluorine) as it is in its handling problems.

Highly desirable, it is nonetheless difficult to prepare in high concentrations and unpredictable in explosive reactions—qualities which have marred much research into its properties and uses. Adequate handling hardware has not been developed.

The instability and toxicity of ozone have given it quite a vicious reputation. But other noxious materials, notably liquid hydrogen and liquid fluorine, have been researched and tamed, to prove their worth. NASA has both done "in house" research and supported contract work, chiefly with the Research Institute of Temple University,

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*Prepared by Mr. C. S. Stokes, Research Institute of Temple University.

in the field of ozone handling and stabilization. This work has led to valuable contributions to the understanding of the ozone hazard.

Since ozone is not handled in the bulk quantities common to most fuels and oxidizers, little is known on the subject. The Research Notes will reflect thinking at NASA's Lewis Research Laboratories and The Research Institute of Temple University.

SOURCE AND PREPARATION

Although the earth's crust consists of oxygen to a degree of 50 percent, much of this oxygen is in combination with other substances. Nevertheless, the atmosphere and the oceans are vast reservoirs of oxygen and are easily prevailed upon to produce ozone.

Ozone can be produced by several methods, but passing electrical discharges through air or oxygen is the most satisfactory process. Bulk production methods involve employing two concentric glass cylinders lined with electrically conductive material in the manner of a capacitor (ozonator). A high electrical potential difference is maintained across the foil layers; as oxygen is passed through a yield, possibly as high as 14 percent, of ozone is obtained. (The most economical yield, however, is usually 2 or 3 percent.) At lower temperatures, yields may reach 90 percent at the temperature of liquid nitrogen. To prepare pure ozone in this manner, a mixture of oxygen and ozone is cooled to $-321°$ F, whereupon the ozone, being more readily condensed, may be obtained in a liquid state almost free of oxygen.

Chemical methods used to produce ozone-rich oxygen are:

1. The decomposition of periodic acid (H_5IO_6) by heat.
2. The autodecomposition of hydrogen peroxide or many of the peracids.

Although ozone liquefaction costs are high at present, large scale production could make ozone much more available.

LABORATORY PREPARATION

As a starting material, the purest oxygen available is used, the so-called "breathing oxygen." In line with the suggestions of the C. A. Thorp patent (U.S. 2,700,648), January 25, 1955, special attention must be given to the elimination of all organic impurities in the ozone produced. This is accomplished by passing a stream of oxygen before the ozonator, through a stainless steel tube containing copper oxide heated to 1292° F. In this tube traces of organic compounds (of the order of a few parts per million) are oxidized to CO_2 and H_2O, which are then absorbed in a tube filled with calcium sulfate, Ascarite, and anhydrone.

The ozonator produces ozone in a concentration of 3–6 percent by volume. The ozone-containing stream is first precooled with a dry ice heat exchange and the O_3 is completely condensed with comparatively small amounts of oxygen in a liquid oxygen trap. The boiling points of ozone and oxygen ($-112°$ C and $-183°$ C) are sufficiently wide that separation of the two can be readily achieved by standard vacuum techniques.

The 100 percent pure ozone is carefully vaporized into a vacuum system of known volume, the pressure recorded, and the ozone then is either used as such or mixed with known volumes of oxygen to prepare any desired mixture.

NATURE OF THE HAZARD

Gaseous, liquid, or solid ozone explodes easily if exposed to heat, spark, flame or shock. When working with highly concentrated ozone, improper handling alone may cause a violent explosion. Furthermore, impurities sensitize the ozone vigorously. Therefore, a knowledge of the properties and safety precautions is very important.

In recent years, ozone has attracted attention as a high-energy chemical with a potential use in powerful propellant and explosive systems. Being an endothermic compound and a highly reactive oxidizer, ozone can burn and detonate by itself and by combination with various fuels. Ozone also represents the simplest combustible and explosive system. When combined with fuels, ozone produces systems with much higher energy content than does oxygen.

PHYSICAL PROPERTIES

At ordinary temperatures, ozone is a gas, light blue in color, and has that characteristic pungent odor from which its name was derived. The odor permits recognition of ozone in concentrations as small as 0.1 ppm.

In the liquid phase, ozone has an indigo-blue color. At temperatures around $-297°$ F liquid ozone may be kept without noticeable decomposition for long periods. Fast warming to the boiling point or rapid cooling causes explosions. Therefore, the liquid ozone must be evaporated or frozen very slowly with appropriate precautions. Liquid ozone can be supercooled readily.

Solid ozone has a deep blue-violet color. A layer of 0.2 to 0.5 mm is transparent, but solid ozone in a layer 1 mm thick is almost opaque. Solid ozone (at $-320°$ F) was compressed to 22.5 atm without any difficulty. Slight impact and slight friction at that temperature did not cause an explosion.

Molecular Weight_____ 48.0
Boiling Point, ° F_____ —169.4
Melting Point, ° F_____ —315.0
Specific Gravity at Boiling Point_____ 1.354
Density, lb/ft³ at Boiling Point_____ 91.15
Vapor Pressures, psi:
     0.0211 at —297.4
     0.479 at —238.0
     16.73 at —166.0
     134.4 at —94.0
     281.0 at —58.0
     664.3 at —4.0
Viscosity at —297.4° F, lb/ft sec_____ 1040
Surface Tension at —297.4° F, lb/ft_____ 263.13×10^5
Critical Temperature, ° F_____ 10.2
Critical Pressure, psi_____ 807.4
Heat of Fusion at Melting Point, Btu/lb mole (est'd)_____ 0.9
Heat of Vaporization at Boiling Point, Btu/lb mole_____ 5328
Heat Capacity, Liquid at Boiling Point, Btu/lb mole ° F_____ 17.0
Heat of Formation at 77.6° F, Btu/lb mole_____ 61,560

CHEMICAL PROPERTIES

Ozone is more soluble in water than in oxygen. It is decomposed rapidly by heat, converting to oxygen. Gaseous ozone is a highly active, irritating, oxidizing substance. It is characterized by strong oxidizing power and by a tendency to revert to molecular oxygen, according to the reaction:

$$O_3 \rightarrow 3/2\ O_2$$
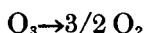
The rate of reaction depends upon the temperature, pressure, and concentration of the ozone. The reaction proceeds slowly at ordinary temperatures, but fairly quickly, even to the velocity of thermal explosion, at elevated temperatures. In addition, the reaction is catalyzed by many sensitizers such as silver or copper. Low temperatures contribute to the conservation of ozone.

Ozone is used in oxidizing organic compounds; it combines with double bonds to form ozonides, which are decomposed by water to give aldehydes, etc.

TOXICITY

Ozone strongly irritates the upper respiratory system. At a concentration of 0.15 ppm ozone in air, the odor becomes just detectable. A disagreeable odor is produced by concentration of 1 ppm and could cause headache and upper respiratory irritation; personnel can avoid the problem simply by leaving the ozone contaminated area. Exposure to high concentrations may cause death from lung congestion and edema, but no systemic effects have been reported following industrial exposures. The accepted threshold limit value is 0.1 ppm in air.

DYNAMIC HANDLING

˙ There is no known method for the safe handling of large amounts of 100 percent pure liquid ozone, but its use in laboratory work can be made safer by knowledge of certain key design criteria.

MATERIALS AND DESIGN

In general, any organic or catalytic material is unsuitable for use with ozone. Laboratory systems can be made of glass using Kel-F lubricant at ground glass joints and stopcocks. For large scale process apparatus where high percentage ozone is used, most stainless steels and aluminum are compatible but must be scrupulously cleaned and passivated with a jet of "on stream" ozonator ozone-oxygen mixture. No material or alloy containing copper should be used.

It could be said that a system must be cleaned as if for fluorine service.

RESEARCH NOTES

The pages that follow reflect the latest research from NASA on the subject of ozone handling. The thinking here is that liquid ozone can be handled and stored best as mixtures of certain compatible compounds. Therefore, this area is subdivided into two areas: Liquid ozone-oxygen and Freon-12-ozone.

LIQUID OZONE-OXYGEN MIXTURES

The potential advantages of liquid ozone as a rocket oxidant have not been exploited because liquid ozone is a high explosive which is easily detonated. One way to make ozone safer is to dilute it with liquid oxygen.

Various viewpoints are extant on what constitutes a safe rocket propellant. A reasonable criterion is that the liquid shall not propagate a brisant detonation even from a high-energy disturbance, which means that knowledge of detonation limits is essential. Understanding of other properties is also important to insure that safe mixtures will not be treated in such a way as to make them unsafe.

A conservative interpretation of detonation experiments indicates that mixtures containing 30 percent or less ozone in liquid oxygen can be run safely in an experimental rocket. Published physical property data, however, show that the temperature of liquid ozone-oxygen mixtures must be properly controlled to avoid danger. Several problems encountered in operating an experimental rocket with liquid O_3-O_2 and gaseous hydrogen are described which shed light on the handling problems of this mixture.

Composition limits of propagation were determined in liquid O_3–O_2 mixtures contained in refrigerated tubes of glass and stainless steel. Initiation was either by spark or by the detonation of a 100 percent ozone booster change.
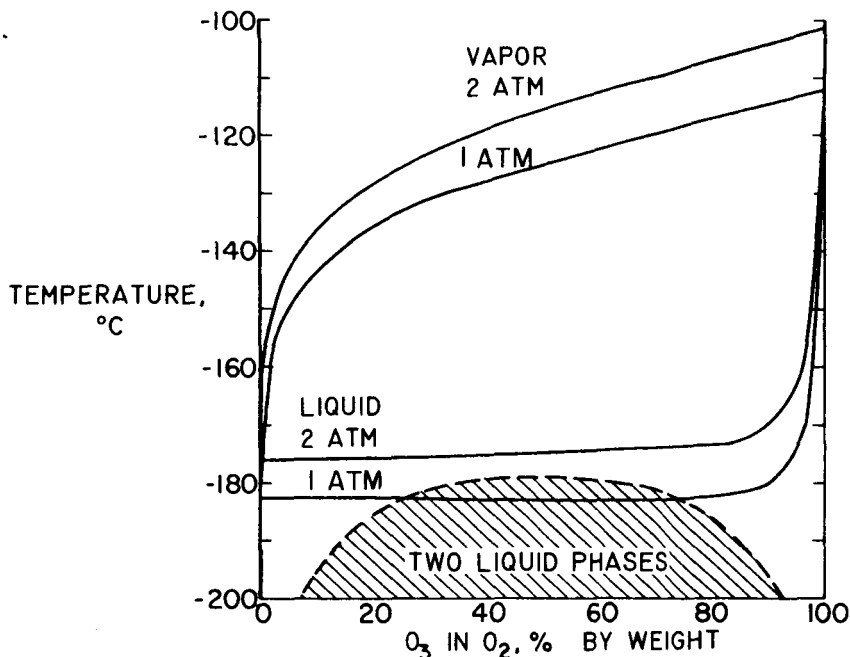
Nature

From about 50 to 100 percent ozone, steady-state Chapment-Jougnet detonations propagate readily from a spark. Small charge diameter and high initial pressure may inhibit these detonations to an extent, but composition (about 50 percent by weight) is the most important limit. With 50 to 35 percent by weight ozone, detonation is still possible from a 100 percent ozone booster charge. Such detonations, however, are inefficient for not all the ozone reacts during propagation. In glass tubes an effect of initial pressure was detected. At high pressures no detonation followed the booster explosion. Near 1 atm there were detonations, but they decayed slowly. This propagation may be attributed to adiabatic compression of tiny oxygen bubbles in the liquid. At low pressure the oxygen in the mixture is near its boiling point.

With 35 percent or less ozone, no brisant propagation was obtained even from the 100 percent booster charge, whether in glass or in metal tubes as large as 11 mm and with initial pressures from 1.5 to 70 atm's. If temperature is properly controlled, 30 percent liquid ozone probably can be run in a well-designed rocket without propagation of brisant detonation even from high-energy sources.

Handling

A safe O_3–O_2 mixture may not stay safe if it is improperly handled. Ozone, because of its physical properties, can inadvertently be concentrated and cause trouble. With the aid of the diagram on page 69, three of the ways ozone can concentrate are explained:

1. High-concentration liquid ozone may condense from a dilute gas. Suppose the gas from an ozonator contained 2 percent ozone and was at 2 atm pressure. The vapor curve for this condition intersects the 2 percent line at about −150° C on the left. The liquid, in equilibrium with the vapor at these conditions, contains about 98 percent ozone. Therefore, a very efficient separation is possible. A small amount of 98 percent liquid ozone could damage a piece of equipment if it detonated.

2. Dilute liquid ozone, on the other hand, may lose oxygen by evaporation if the temperature is increased. Suppose a liquid O_3–O_2 mixture at 1 atm is allowed to warm to −170° C which is only 13° above the boiling point of oxygen. The concentration of liqiud ozone would reach 96 percent.

Phase diagram of ozone-oxygen.

3. The existence of a two-liquid-phase region provides another danger. If the temperature and composition are in a region where the liquid will separate into two phases, one will be more concentrated than the other. The composition of the two phases will be read from a curve. As an example, at $-183°$ C, the boiling point of liquid oxygen, 25 percent ozone is about the maximum which will stay in one liquid phase.

STORAGE OF OZONE IN FREON-12

Ozone has been shown to be readily soluble in Freon–12 (dichlorodifluoromethane) at temperatures as low as $-238°$ F. Freon-12-ozone solutions of up to 15 wt percent O_3 are stable when kept at $-108°$ F (dry ice) and under a helium overpressure of at least 1000 psig. Sensitivity tests show that the solutions are insensitive to mechanical, electrical and high brisant shock.

The preparation and handling of a Freon-12-ozone solution was accomplished in the following manner:

A stainless steel tank of approximately 450 cubic inches with appropriate stainless steel inlet and outlet valves was used for the large scale preparations. The inlet valve had attached to it a dip tube which

went to the bottom of the tank. A series of holes was drilled in the side of the dip tube, and the end was sealed off, providing a system for bubbling ozone-oxygen through the Freon–12.

The tank and accessories were passivated for the ozone-Freon mixture by passing 3 to 4 percent ozonated oxygen through them for a period of 5 hours. The ozone tank was filled with 24.6 lbs of Freon–12 and immersed in a liquid nitrogen cooled Freon–12 bath. The inlet and outlet valves were closed, and the Freon bath was cooled down to $-258°$ F $\pm 4°$ in a period of six hours. At this point the ozonator was turned on and allowed to stabilize for a period of one hour under the flow conditions which were to be used in the ozonization of the Freon–12. During this time, (to insure a constant temperature in the bath) a check was made on the temperature of the tank by means of thermocouples. Having a variation of no more than $4°$ F, the ozonated oxygen from the ozonator was allowed to flow into the ozone tank. The ozone inlet concentration varied from 3.04 to 3.80 percent, and the outlet ozone concentration varied from .05 to 1.1 percent. After several initial disturbances, the oxygen flow steadied to 10.6 l./min. By integrating the inlet and outlet ozone concentrations from the ozone tank, an accurate concentration of the dissolved ozone in the Freon-12 can be determined at any point during ozonization. The ozonization was stopped after 27¾ hours with a final ozone concentration of 8.0 percent (by weight) in Freon–12. It was found that the Freon-12 also contained approximately 2 percent dissolved oxygen. At this point the ozonator was turned off, and the ozone tank was disconnected from the ozonator. The tank was then connected to a helium pressurization system which included a dry ice-cooled trap. The pressure was built up by a series of line entrapments to a pressure of 950 pounds. The tank was then removed from the Freon bath and placed in dry ice in the storage box. Dry ice was placed completely around the tank, and the box was closed and carried out to the test area, approximately 150 yards from the preparation site. A pressure test was made on the tank after 2½ hours, and the final pressure was found to be 1700 psig. This procedure was repeated many times without problems.

Storage tests were performed where temperature and pressure were monitored continuously. No decomposition of the ozone was noted over an eight-day period. It was concluded from these tests that ozone-Freon–12 solutions can be stored for long periods of time provided they are kept at $-108°$ F and under a 1000 psig helium overpressure.

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Nitrogen Tetroxide

INTRODUCTION

Nitrogen tetroxide, like fluorine, is an oxidizer. Quite chemically reactive, it possesses those desired characteristics, that, when combined with a high-energy fuel such as UDMH/hydrazine, qualify it for use in the Air Force Titan II I.C.B.M. and Titan III Launch Vehicle. Nitrogen tetroxide has the desired feature of storability and the same high-energy level with such oxidizers as liquid oxygen or liquid fluorine. Together with the UDMH/hydrazine fuel, this propellant combination may be stored as a hypergolic (self-igniting) propellant in a missile system for several months. This feature provides a state-of-readiness approaching that of a solid-fueled booster, and pound for pound, the nitrogen tetroxide combination will provide a greater energy level.

Nitrogen combines with oxygen to form a variety of oxidizer compounds which are of interest in propellant systems. Nitrogen tetroxide has been the most used primarily because of its energy of reactivity and its storability with fewer handling problems.

Commercially, nitrogen tetroxide is used as a nitrating agent in the production of nitric acid. It is also employed as an oxidizing agent and as a catalyst.

SOURCE AND PREPARATION

Nitrogen tetroxide, N_2O_4, is also known as dinitrogen tetroxide, nitrogen peroxide, or "liquid dioxide." It is sometimes said to be a "polymer" of nitrogen dioxide, NO_2, in which form it does indeed exist at a higher temperature. At intermediate temperatures there is an equilibrium between the two forms:

$$N_2O_4 \rightleftharpoons 2NO_2$$

There are several methods of producing nitrogen tetroxide; three of the most important are:

1. Catalytic oxidation of ammonia (NH_3).
2. Oxidation of nitrosyl chloride (NOCl) when it is formed from salt and nitric acid and then oxidized with oxygen.

3. Decomposition of metal nitrides with nitric acid.

In each case nitrogen dioxide is formed and polymerized into nitrogen tetroxide. Such production is limited but the process could be rapidly expanded by use of existing large-scale nitric acid facilities.

NATURE OF THE HAZARD

At normal temperatures and pressures (68° F, one atm), nitrogen tetroxide is an equilibrium liquid mixture of 84 percent nitrogen tetroxide and 16 percent nitrogen dioxide. The mixture contains about 30 percent nitrogen and 70 percent oxygen. The position of the equilibrium between nitrogen tetroxide and nitrogen dioxide is dependent upon the temperature and physical state involved. In the solid state, nitrogen tetroxide is colorless, but as the temperature is increased it dissociates into nitrogen dioxide that is a reddish-brown gas. Thus, the liquid tetroxide is brown, although it contains less than 0.1 percent nitrogen dioxide. The color of the gas becomes more intense with rising temperature. At 212° F, the tetroxide is 90 percent dissociated into the dioxide.

As an oxidizer, half of its oxygen can be utilized under mild conditions, and under more vigorous conditions all of the oxygen is available. Nitrogen tetroxide, of great interest to NASA as a storable liquid oxidizer, is hypergolic with hydrazine, cyclic hydrazine, aniline, toluidine and oxylidine, and with furfuryl alcohol, cyclopentadiene, pyrocotichol and the metal carbonyls.

PHYSICAL PROPERTIES

Molecular Weight	92.016
Boiling Point, ° F	70.07
Freezing Point, ° F	11.84
Specific Gravity at 68° F	1.337
Density 68° F, lbs/ft³	90.34
Specific Gravity of Gas, 70° F and 1 atm air=1	3.40
Vapor Pressure 32° F, psia	5.1
Vapor Pressure 70° F, psia	14.7
Vapor Pressure 104° F, psia	35.3
Viscosity at 68° F, lb/ft-sec	2.84×10^{-4}
Heat of Fusion, 11.8° F, Btu/lb	68.5
Heat of Vaporization, 70.07° F, Btu/lb	17.8
Heat of Formation, Liquid, 77° F, Btu/lb—mole	−12,240
Heat Capacity 62° F, Btu/lb	0.367
Odor	Very Unpleasant
Critical Point	316° F. 1470 psia

CHEMICAL PROPERTIES

Nitrogen tetroxide of commercial purity is stable at ordinary temperatures; it is considered a corrosive oxidizing agent. Even at high temperature it exhibits only the dissociation into nitrogen dioxide. The vapor pressure of nitrogen tetroxide at 100° F is 17.6 psig, and at 140° F, 62.3 psig; therefore, refrigeration is not required to keep nitrogen tetroxide in liquid form. Anhydrous nitrogen tetroxide may be safely stored in moderate pressure vessels; its storability is favored by virtue of its noncorrosiveness to steel under ordinary conditions. The low viscosity of liquid nitrogen tetroxide ranging from 0.5 centipoise at 40° F to .06 centipoise at 280° F gives desirable flow characteristics.

TOXICITY

Like most high-energy oxidizers, nitrogen tetroxide exhibits a disadvantage by virtue of its extreme chemical reactivity.

In liquid form, it has been found injurious to animal tissue, resulting in severe burns to skin and eyes. But the most serious health hazard results from inhalation of the vapors. The main danger is a delayed pulmonary edema, the filling of the lung spaces with fluid, resulting in an inability of the lungs to transport oxygen. This condition may not develop until a day later. The initial symptoms of such poisoning are slight, and the initial warning may thus go unnoticed. The color of the fumes is not a realiable guide to toxic hazard. The Threshold Limit Value has been set at 2.5 ppm (9 mg per cubic meter).

Chronic exposure to nitrogen tetroxide fumes at low concentrations may result in decay and wearing of the teeth plus irritation of the respiratory tract. Bronchitis, bronchiectasis, and secondary pulmonary emphysema may result. If the liquid is splashed on skin or eyes, it must be removed immediately by flushing the affected area with large amounts of water.

DYNAMIC HANDLING

Any organic material that may be readily oxidized is unsatisfactory for use in the handling and storage of liquid nitrogen tetroxide. Pure moisture-free nitrogen tetroxide is not corrosive to most common metals, but nitrogen tetroxide containing more than 0.1 percent moisture will cause corrosion. Selection of a material of construction is governed by the moisture content of the nitrogen tetroxide. The material reacts with water to form nitric acid which is more corrosive to most materials of construction than the nitrogen tetroxide itself. All nitrogen tetroxide systems and components must be absolutely dry.

MATERIALS AND DESIGN

The following materials are considered compatible with nitrogen tetroxide:

Aluminum Alloy Number 1100
Aluminum Alloy Number 5052
Aluminum Alloy Number 6061
Aluminum Alloy Number 6066
Aluminum Alloy Number 356
Aluminum Alloy Number B356
Aluminum Alloy Tens 50
Stainless Steel AISI 300 series
Stainless Steel AISI 400 series
Stainless Steel AM–350
Stainless Steel AM–355
Stainless Steel 17–4 PH
Stainless Steel 17–7 PH
Iron-Base Superalloy A–286
Iron-Base Superalloy 16–25–6
Inconel X
Teflon
Teflon filled with asbestos or glass
Teflon-fiberglass (LNP)
Viton A
Viton B
NA2–205–2 (Alochlor–1254 Moncanto)
Graphite (dz)
Molycote Z (Binderless)

Teflon is listed as a compatible material, but a tendency for Teflon to swell in liquid N_2O_4 has been noticed. This tendency is particularly troublesome when Teflon is used as packing in control valves.

The following materials have been found to be satisfactory for *limited service* in nitrogen tetroxide:

Mild Steels
Fluoro-Silicone Rubber (LS–53 series)
Polyethylene
Keroseal
Saran

The following materials are *incompatible* with nitrogen tetroxide and must *not* be used:

Aluminum Alloy Number 2024	Cadmium
K–Monel	Nickel
Brass	Micarta
Bronze	Mylar
Silver	Buna N
Copper	Hypalon
Titanium	Oxylube
Zinc	

HANDLING

When transferring liquid nitrogen tetroxide, pumping is preferable to overpressuring the liquid with inert gas because of the reduced possibility of introducing moisture. If the gas pressurizing method must be used, dry compressed air or gaseous nitrogen is recommended. In any pumping operation a mechanical seal must be used around the drive shaft of the pump to prevent leakage. A magnetically driven seal-less pumping unit is also permissible.

HARDWARE

Valving should be constructed of stainless steel. Teflon packed needle valves are acceptable, but bellows-type packless valves are preferred.

Piping and fittings should be weld connected wherever possible especially on high-pressure liquid lines. If it is necessary to use threaded connections, Teflon thread sealant is preferred. Flexible hosing should be lined with Teflon or stainless steel as other materials may become hard and brittle after exposure.

Motors, starters, switches, receptacles, etc., are subject to severe corrosion damage if exposed to nitrogen tetroxide vapors. Vapor-tight electrical equipment must be used to prevent internal damage and subsequent failures. Hermetically sealed electrical components have been used on liquid installations where space limitations prohibit the use of conventional vapor tight apparatus.

PREPARATION

All the components of a nitrogen tetroxide system must be properly prepared prior to installation. Preparations are twofold: thorough cleaning, and chemically inerting the pieces against the nitrogen tetroxide (passivating). Pieces fabricated of stainless steel and aluminum alloys can be degreased in trichloroethylene or a warm mild alkali solution.

Welded or heat-treated components usually must be descaled. The descaling of stainless steel components can be accomplished by etching the part in a water solution of 3 to 5 percent hydrofluoric acid (HF) and 15 to 20 percent nitric acid (HNO_3).

Passivation

The passivation procedure for the components of a nitrogen tetroxide system is somewhat less vigorous than for the fluorine oxidizer. Fifty percent nitric acid is used for stainless steels and aluminum alloys. Approximately one-half hour for stainless steel and one hour for aluminum alloys is recommended. After rinsing thoroughly with

distilled water the item should be dried by purging with nitrogen gas or heating in an oven to approximately 150° F.

If the item is not to be used immediately, it must be stored in such a way as to prevent contamination. Large components can be sealed and pressurized with dry nitrogen to approximately 10 to 15 psig. Smaller parts can be stored in clean plastic containers.

Leaks and Spills

The most important consideration for the safe handling of nitrogen tetroxide is prevention of spills and leaks, which are the main cause of facility damage and personnel poisoning.

The integrity of the plumbing and hardware is of vital importance. Safety factors that should not be overlooked follow:

1. The use of only compatible construction materials.
2. The reduction of mechanical joints to a minimum. Every flare fitting, flange fitting, pipe fitting, etc., is a potential leak point.
3. The elimination of liquid traps.
4. The provision for a permanently connected inert gas purging system.
5. The allowance for a vent scrubber or high vent stack.

In case of a spill, or a fire fed from a spill, first stop the flow of nitrogen tetroxide, preferably by closing a valve remote from the spill or fire area. If a small amount of propellant has spilled, the propellant may be allowed to vaporize to depletion. The control techniques applicable to large spills depend upon maximum tolerable propellant vaporization rates. A minimum vaporization rate is experienced when the nitrogen tetroxide is allowed to vaporize. However, large amounts of vapor are still being generated over a relatively long period of time. Deluging the spill area with large amounts of water will dilute the propellant very quickly; however, the vaporization rate is greatly increased.

HAZARD CONTROL

Chemical reactivity takes the form of fire or explosion. Nitrogen tetroxide by itself will not burn but will actively support combustion. The smoke and fumes from these fires are toxic and should be approached from upwind.

Even though nitrogen tetroxide is an hypergolic-type oxidizer, mixtures with non-hypergolic fuels present an explosion hazard. The possibility of pressure-vessel ruptures always exists at elevated temperatures, where the vapor released can form explosive mixtures with fuel vapors in confined spaces. Consequently, the material must be stored and handled in well ventilated areas remote from fuel storage areas.

Fire control is handled essentially the same as spill control. The water deluge technique is effective under these conditions since it not only controls the spill but may reduce the temperature of material exposed to the fire.

Safety Equipment

Appropriate equipment must be provided for personnel and facility safety. Facility safety equipment should consist of emergency showers, eye wash fountains, a water deluge system, fire blankets, first aid kit, fire hoses, and fire extinguishers. If poorly ventilated areas are unavoidable, nitrogen tetroxide detectors are a necessity because the color of the gaseous material becomes visible at 50 ppm whereas the maximum allowable concentration is 5 ppm.

Personnel should operate in pairs or larger groups and be properly dressed in completely impervious and protective safety clothing.

After a fire or spill the area must be decontaminated by flushing or neutralizing the remaining nitric acid. Ordinary water or a mild alkali solution can be used. The removal of a component from a nitric acid system must be preceded by a thorough gas purge to remove any residual propellant. If the removed component is to be reused without service or modification, no further decontamination operations are required; otherwise the removed component is purged thoroughly with water and dried in a gaseous nitrogen stream.

SHIPPING

The I.C.C. has approved shipment of nitrogen tetroxide in quantities up to 10,000 gallons. The material is classified by the I.C.C. as a "Class A Poisonous Gas."

N_2O_4 is available in quantities from 10 to 156 lbs in seamless steel cylinders, 2,000 lbs in forged steel cylinders, and 10,000 gallons in tank cars.

RESEARCH NOTES

NASA's interest in nitrogen tetroxide is reflected in Chapter 7 on hydrazine compounds, where study of the combination of these two as a storable propellant is reported. Applicable notes pertaining to nitrogen tetroxide may be found in that chapter.

Hydrazine Compounds

INTRODUCTION

The promise that hydrazine and its compounds would be among the first high-energy propellants in common usage has already been realized. Hydrazine, unsymmetrical dimenthylhydrazine, and monomethylhydrazine have been tested as fuels and found to provide over 250 impulse seconds of thrust; they have demonstrated their launch boost capability, both singly and as mixed compounds.

Hydrazine has been known for more than 70 years, but has been in large-scale production only in recent years. The Germans used it during World War II as a torpedo propellant and later for jet aircraft fuels. Following the war, this country became interested in it as a rocket fuel. It has the reputation of being a storable fuel, because of its wide range ambient thermal stability. The Titan II I.C.B.M. uses hydrazine/UDMH (unsymmetrical dimethylhydrazine) because of its long range storage capability, with nitrogen tetroxide as its corresponding oxidizer. The specific impulse of just under 300 seconds is not altogether prime, but it does surpass that of solid propellants in an identical application.

Recently, the methyl derivatives of hydrazine have been found to exhibit performance characteristics similar to those of hydrazine, with physical properties more favorable to use as a propellant. Coming under the classification of an organic propellant, these methyl derivatives of hydrazine, such as the simplest alkyl homologs, contain a minimum amount of carbon atoms and yet provide the highest hydrogen-to-carbon ratios.

Unsymmetrical dimethylhydrazine, which has a freezing point below hydrazine and a performance approaching that of hydrazine, is a hydrazine derivative. Monomethylhydrazine (MMH) is similar to hydrazine in its catalytic stability, but is not as stable as UDMH, which has found popular acceptance in upper stages of NASA's famed utility boosters, Thor-Delta and Thor-Agena. MMH may be used in

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the Apollo service module because of its stability over a wider temperature range and resultant weight savings on insulation materials.

A 50–50 blend of UDMH and hydrazine, known simply as "Aerozene," is the most commonly used fuel at present. This blend combines the prime performance characteristics of hydrazine with the wide range of thermal stability of UDMH.

Hydyne is another blend: 60 percent UDMH and 40 percent diethylenetriamine. This mixture provides good specific impulse characteristics of over 250 seconds, but its usage has been limited to short-range liquid propellant rockets.

SOURCE AND PREPARATION

Two processes may be used in the preparation of hydrazine. One involves reacting sodium hypochlorite with an excess of ammonia at 160° C which results in a dilute (1–2 percent) product; some still weak hydrazine is yet recovered by flash boiling. This dilute product is fractionated to produce a hydrate composition. (The Raschig Method.) As an alternative, hydrazine may be recovered by precipitation from the synthesis product as monohydrazine sulfate. The sulfate must be neutralized with caustic soda to release hydrazine hydrate, which in each case must be distilled to complete the manufacture of anhydrous hydrazine. A second process is a slight modification of the Raschig process in which urea is substituted for ammonia. It is oxidized by caustic soda, resulting in the hydrazine hydrate.

Amines may be prepared by three processes:
1. Alkylation of hydrazine.
2. Synthesis of alkyl hydrazines via chloramine.
3. Reduction of nitrosodialkylamine.

NASA's present requirements for such storable fuels as these hydrazine compounds are small in comparison to requirements for the major booster fuels, and there is constant competition with solid fuel. Hydrazine compounds, nevertheless, are expected to share a major part of the load in the realm of storable propellants; the Apollo program is second to the Titan II I.C.B.M. program in use of hydrazine compounds.

NATURE OF THE HAZARD

HYDRAZINE

Hydrazine, N_2H_4, is a clear, oily, water-white liquid. The material is a strong reducing agent, weakly alkaline, and very hygroscopic. It has an odor similar to ammonia. If the material is exposed to air on a large surface, such as a rag, spontaneous ignition may result from the heat evolved by oxidation with atmospheric oxygen.

Physical Properties

Molecular Weight_____ 32.05
Boiling Point, ° F_____ 235.9
Freezing Point, ° F_____ 34.8
Specific Gravity at 68° F_____ 1.008
Density, lbs/ft^3 at 68° F_____ 62.93
Vapor Pressure, psia at 68° F_____ 0.2
Viscosity, lbs mass/ft-sec_____ 6.54×10^{-4}
Surface Tension, lbs force/ft_____ 0.00456
Critical Temperature, ° F_____ 716
Critical Pressure, psia_____ 2130
Critical Density, lbs/gallon_____ 1.9
Flash Point (open cup) ° F_____ 100–126° F
Autoignition Temperature ° F_____ 518
Heat of Formation (liquid) at 77° F, Btu/lb mole_____ 21,600
Heat of Fusion, Btu/lb at 34.8° F_____ 170
Heat of Vaporization, Btu/lb at 77° F_____ 602
Heat Capacity at 68° F, Btu/lb ° F_____ 0.7358

Chemical Properties

Hydrazine is a highly polar electrolytic solvent and is soluble in water, methanol, unsymmetrical dimethylhydrazine, and ethylene diamine but is insoluble in ethers and hydrocarbons.

Hydrazine is a stable liquid under extremes of heat and cold. It contracts upon freezing so that there is no damage to storage vessels. Thermal decomposition begins at about 320° F but may occur at lower temperatures in the presence of such catalysts as copper or molybdenum. Liquid hydrazine is stable to shock but its vapor propagates detonation waves within the flammable limits.

Although aqueous solutions of hydrazine are used in various commercial applications, the anhydrous form has been limited thus far to the field of rocket propellants. As a propellant, the performance of anhydrous hydrazine surpasses that of such common fuels as kerosene, unsymmetrical dimethylhydrazine, ammonia, and monomethylhydrazine.

Commercial anhydrous hydrazine boils at about 239° F. It can be stored in low-pressure vessels for long periods of time, although a gaseous nitrogen blanket must be added to prevent oxidation.

Toxicity

Hydrazine is very toxic; inhalation of even dilute concentrations should be avoided. Liquid hydrazine, if spilled onto the skin or into the eye, can cause severe local damage or burns. It can also penetrate the skin to cause systemic effects similiar to those produced when the compound is swallowed or inhaled. Exposure to hydrazine can also result in dermatitis.

The threshold limit value which has been adopted by the American Conference of Governmental Industrial Hygienists is 1 ppm, which is the TLV for repeated eight-hour exposures. The minimum for odor detection is about 3 to 5 ppm. Since hydrazine vapors cause olfactory fatigue, the detection of hydrazine by odor can be used only initially as a first warning.

In chronic exposure tests of animals to hydrazine vapors, inhalation produced lung damage, inflammation of the liver, inflammation of the kidney, anorexia (loss of appetite), loss of body weight, tremors, weakness, and after prolonged exposure, convulsions followed by death. Lung congestion and edema appear to be the principal effects of hydrazine. Some breakdown of red blood cells has been noted in animals.

Liquid anhydrous hydrazine is very stable and nonexplosive. Hydrazine vapors present a serious fire hazard, although in the absence of decomposition catalysts, it has been heated above 500° F with little decomposition.

Liquid hydrazine at 104° F exerts sufficient vapor pressure to support a 4.7 percent hydrazine in air mixture which is flammable: 4.7 percent and 100 percent by volume are the limits of flammability.

UDMH

UDMH (unsymmetrical dimethylhydrazine) is a clear, water-white liquid with an ammoniacal odor. The vapor reacts very slowly with air at ambient temperatures to form traces of several products; this is not of practical significance with regard to normal storage and handling.

Physical Properties

Molecular Formula_____ $(CH_3)_2 NNH_2$
Molecular Weight_____ 60. 08
Freezing Point, °F_____ −71. 0
Boiling Point, °F_____ 146. 0
Critical Temperature, °F_____ 482
Critical Pressure, atms_____ 53. 5
Density (liquid) at 77° F, lbs/gal_____ 6. 56
Vapor Pressure at 77° F, atms_____ 0. 206
Viscosity (liquid) at 77° F, centistokes_____ 0. 647
Heat Capacity (liquid) at 77° F, Btu/lb ° F_____ 0. 653
Heat Capacity (gas) at 77° F, Btu/lb ° F_____ 0. 377
Thermal Conductivity (liquid) at 77° F, Btu-ft/hr-ft² ° F_____ 0. 12
Heat of Fusion (Freezing Point), Btu/lb_____ 72
Heat of Vaporization (Boiling Point), Btu/lb_____ 251
Heat of Formation (liquid) 77° F, Btu/lb_____ 381
Spontaneous Ignition Temperature in air at 1 atm, ° F_____ 482
Spontaneous Ignition Temperature in air at 200 psi, ° F_____ 298
Flammability Limits in air, 100% by vol_____ 2 to 90

Chemical Properties

•UDMH is miscible with water, ethanol, petroleum fuels and various amine fuels including ethylene triamine and hydrazine. It is not shock sensitive and is stable to heat and catalytic decomposition. The vapor in air is flammable over a wide concentration.

Due to its high vapor pressure and wide range of flammability there is always the possibility of explosive mixtures forming over the liquid. Although the liquid is not sensitive to shock or friction, UDMH-air mixtures can be exploded by an electric shock or open flame. For this reason a blanket of nitrogen should be used wherever practical.

Toxicity

UDMH is described as moderately toxic. UDMH is mildly irritating to the skin and eyes; it can penetrate the skin to cause systemic toxicity. However, it is not as dangerous as hydrazine in these respects. Since tremors or convulsions predominate on short exposure, UDMH appears to be a more potent stimulant than hydrazine. Chronic poisoning is characterized by anemia. UDMH appears to have little or no capability for causing liver damage. The Threshold Limit Value for chronic exposure to UDMH by vapor inhalation is 0.5 ppm by volume.

Although UDMH is not a Class B poison by the ICC classification of hazards, compared to other well-known propellants it is more toxic than the hydrocarbons, the alcohols and ammonia, and less toxic than the boranes.

MMH

MMH (monomethylhydrazine) is a clear, water-white liquid with an ammoniacal odor. It will absorb CO_2 and water from the air. MMH is a volatile liquid and more toxic than hydrazine or UDMH.

Physical Properties

Molecular Formula	CH_3NHNH_2
Molecular Weight	46.075
Freezing Point, ° F	−62.5
Boiling Point, ° F	192.5
Critical Temperature, ° C	312
Critical Pressure, atm	81.3
Critical Density, g/ml	0.29
Density (liquid) 77° F, lbs/gal	7.29
Vapor Pressure 77° F, psia	0.9598
Viscosity (liquid) 77° F, centistokes	0.882
Heat Capacity (liquid) 77° F, Btu/lb, ° F	0.700
Heat Capacity (gas) 77° F, Btu/lb, ° F	0.369
Heat of Fusion, Btu/lb	97.3
Heat of Vaporization 77° F, Btu/lb	376.9
Heat of Formation (liquid) 77° F, Btu/lb	496

Chemical Properties

MMH is stable up to its boiling point only when kept out of contact with oxygen. MMH is not sensitive to impact or friction. It is more stable than hydrazine on mild heating and similar to hydrazine in its sensitivity to catalytic decomposition.

The fire and explosion hazards are similar to those of hydrazine.

Toxicity

MMH is more toxic than hydrazine. LC^{50} (rats exposed for four hours) of MMH is 74 ppm as compared to 570 ppm for hydrazine.

LC^{50} is defined as a figure pertaining to the toxic concentration which kills 50 percent of a group of test animals. Detection of the odor of MMH should offer warning since the median concentration of 1–3 ppm is lower than the LC^{50} value. MMH was found to produce hemolysis and elevated temperature in exposed dogs.

The local effects due to acute exposure to MMH are similar to those effects observed for hydrazine.

MMH produces destruction of the red blood cells and stimulates the central nervous system to a greater extent than the other hydrazines.

DYNAMIC HANDLING

The procedures for handling hydrazine, UDMH, MMH, and other hydrazine derivatives and compounds are for the most part identical.

MATERIALS AND DESIGN

The following materials have been found to be compatible with hydrazine:

Aluminum Alloy Number 1100	Stainless Steel 321
Aluminum Alloy Number 2014	Stainless Steel 347
Aluminum Alloy Number 2024	Stainless Steel 1707 PH
Aluminum Alloy Number 4043	Inconel
Aluminum Alloy Number 5052	Inconel-X
Aluminum Alloy Number 6061	Chromium Plating
Aluminum Alloy Number 6066	Kel-F
Aluminum Alloy Number 356	Teflon
Aluminum Alloy Number B356	Graphite
Aluminum Alloy Tens 50	Dow Corning Number 11
Stainless Steel 304	Sinclair L743

Stainless Steels AM-350 and AM-355 and Iron-Base Superalloy A–236 contain over 0.5 percent molybdenum and should not be used at temperatures above 160° F.

Copper, nickel, and Johns-Manville Packing Number 76 are satisfactory only for limited service, and are generally avoided. Carbon steels are to be avoided, especially with the fuel blends.

Comprehensive compatibility data are not available for MMH, but due to the similarity in catalytic oxidation for MMH and hydrazine, those metals found satisfactory for hydrazine service should suffice for MMH service. In addition, the catalytic sensitivity of MMH recommends that stainless steels containing 0.5 percent molybdenum, Hastalloys, monel, zinc, lead, copper, copper alloys, and iron should not be used on contact with MMH.

All systems either for static or flow conditions must be dry and leakproof, fabricated of compatible materials, and cleaned before the material is introduced. Transfer and storage systems must be free of air, moisture, mist, and contamination because the material reacts with air, metal oxides, and oxidizing agents.

CLEANING

After fabrication, system components must be cleaned, descaled, and made chemically inert before installation. Components can be cleaned in trichloroethylene or a warm, mild alkali solution. Stainless steel components can be descaled by means of etching with an aqueous solution of three to five percent hydrofluoric acid and 15 to 20 percent of nitric acid for approximately 60 minutes.

To passivate or chemically inert stainless steel components, it is necessary to immerse them in 50 percent nitric acid for 30 minutes. Passivation procedures are notably less stringent for the amines than for fluorine or fluorine containing oxidizers.

Obviously items that have been prepared for hydrazine service should be stored or packaged to prevent recontamination.

HANDLING

Hydrazine can be transferred by pressurizing the container with dry nitrogen or other inert gases, or by connecting a transfer pump in the discharge line. Pump construction materials must be compatible. Both methods have been proven successful.

Leaks and Spills

The prevention of spills and leaks is important in handling the material. Spills and leaks present a hazard from both poisoning and fire.

The integrity of the system is important. Some basic design considerations are as follows:
1. Reduce mechanical joints to a minimum.
2. Consider maximum pressure in system design.
3. Eliminate low lying liquid traps wherever possible.
4. Provide an inert gas purge system.
5. Install high stack or scrubber for vent.

Hazard Control

Since hydrazine presents a definite fire hazard, all means of fire prevention should be utilized. The flammability of the vapor may be reduced by diluents. The lower flammability limit may be raised from 4.7 to 38 percent when nitrogen is used as the diluent or 37 percent when helium is used. Following a leak or spill, the hydrazine should be deluged with large amounts of water to assure that it is diluted below 40 percent, such solutions being non-combustible.

After a spill or fire, the area must be decontaminated. (Decontamination also involves the removal of hydrazine from equipment that is to be serviced, inspected, or replaced.) Handling or storage areas, following a spill or fire, must be decontaminated because of the toxicity and possible reignition hazard. The area or component can be decontaminated by washing thoroughly with water. Components should be purged dry with nitrogen gas after decontamination.

Hydrazine fires are best controlled by deluging them with copious quantities of water. The water should be applied in the form of a spray in preference to water fog which is less effective due to increased vaporization of fire droplets in the flame.

Personnel

The toxicity and chemical reactivity of hydrazine dictate that suitable safety equipment be available for the protection of storage areas and operating personnel. Safety equipment should include showers, eye wash fountains, first aid equipment, water spray deluge systems, fire hoses, and fire blankets. Impervious clothing is a must for personnel protection.

RESEARCH NOTES

Hydrazine has been known and used as a fuel for many years. Its handling peculiarities are well known and have been researched to the point that it appears that about everything worthwhile about hydrazine has been generated.

This is not true of hydrazine derivatives and mixtures, and seemingly hydrazine has been found lately to be the "mother" of a number of new fuels. Of course, MMH and UDMH are not exactly new, but attention has been directed only recently to their future roles in space propellant technology. The following selected abstracts may be of some interest, therefore, to a number of prospective users; in any case, hydrazine has certainly graduated from its application as a "torpedo propellant."

BIBLIOGRAPHY

FRIEDMAN, R., ET AL., "A Study of Explosions Induced by Contact of Hydrazine-type Fuels with Nitrogen Tetroxide," Atlantic Research Corp., Alexandria, Va., 1962.

The mechanism of explosions which may result when a hydrazine-type liquid is brought into contact with liquid nitrogen tetroxide was studied. Falling droplet experiments showed correlation between distance of fall and probability of explosion. Sudden injection of one liquid into the other, with high-speed photography, gave nonreproducible results. Occasional explosions occurred, preceded by bubble formation. Alternate theories of the explosion phenomenon are discussed.

LUCIEN, H.; AND PINNS, M. L., "The X-Irradiation of Hydrazine and 1,1-dimethylhydrazine," NASA TN D–2452, 1964.

This study is a continuation of an effort to determine the effects of ionizing radiation on the space storability of chemical rocket propellants. The total doses of X-rays used is representative of that expected through 0.015 inch of stainless steel over a period of about two years at 0.6 to 1.0 astronomical units from a quiet sun.

Hydrazine and 1,1-dimethylhydrazine were radiolyzed at room temperature by using about 1 gram of liquid or $\frac{1}{2}$ to 2 liters of vapor at room-temperature vapor pressure. A tungsten-target X-ray source operating at 300 kilovolts and 6 to 8 milliamperes (0.1 to 1.0 AU) was used at intensities of 1×10^2 to 1×10^3 roentgens per minute to give total doses of 4.1 rads to 2.3×10^6 rads. The amounts of decomposition were dependent on total dose and independent of dose rate. In the case of hydrazine vapor, the decomposition was also directly related to surface area. There was a lesser surface effect with liquid hydrazine, but this variable was not studied for 1,1-dimethylhydrazine. The order of decreasing sensitivity to X-radiation is as follows: hydrazine vapor, 1,1-dimethylhydrazine vapor, 1,1-dimethylhydrazine liquid, and hydrazine liquid. The decomposition products of hydrazine were nitrogen, hydrogen, ammonia, and unidentified products. The same products plus methylamine, dimethyl-amine, and hydrazine were found from the decomposition of 1,1-dimethylhy-drazine. In addition, the 1,1-dimethlyhydrazine underwent postirradiation changes. Values for G (number of molecules of sample decomposed per 100 ev of absorbed energy) of the order of 10^6 suggest that the vapor-phase decompositions are chain reactions.

MARKELS, M., JR., ET AL., "A Study of Extinguishment and Control of Fire Involving Hydrazine-Type Fuels with Air and Nitrogen Tetroxide," Atlantic Research Corp., Alexandria, Va., 1962.

Burning rates, extinguishing agents, and extinguishment mechanisms were determined for open pan fires of hydrazine, unsymmetrical dimethylhydrazine (UDMH), JP–X. A 50–50 mixture of hydrazine and UDMH oxidized by air and N_2O_4 was studied in open pans and in a 1/50 scale model of a Titan II silo. Bicarbonate-based dry chemicals extinguished the pan fires promptly, and with the least weight of agent. Water extinguished the fires by diluting the fuel surface. Coarse spray and alcohol-type foams were effective forms of water application. After extinguishment by dilution, the fires could not be reignited. Water spray was not effective against JP–X fires. Specific rates of application of selected agents under various fire conditions are given. The amine fuels (with the exception of JP–X, which was not tested) exploded hypergolically on contact with liquid N_2O_4 in about half the tests.

ORDIN, P. M.; AND MILLER, R. O., "Experimental Performance of Chlorine Trifluoride-Hydrazine Propellant Combination in 100-Pound-Thrust Rocket Engine," NACA RM E9F01, 1949.

PENNEMAN, R. A.; AND AUDRIETH, L. F., "Quantitative Determination of Hydrazine," *Anal. Chem.*, vol. 20, no. 11, pp. 1058–1061, 1948.

ROLLBUHLER, R., AND TOMAZIC, A., "Comparison of Hydrazine—Nitrogen Tetroxide and Hydrazine—Chlorine Trifluoride in Small-scale Rocket Chambers," NASA TN D–131, 1959.

SPAKOWSKI, A. E., "The Thermal Stability of Unsymmetrical Dimethylhydrazine (UDMH)," NASA Memo 12–13–58E, 1958.

Rocket-powered flight of recoverable vehicles with the attendant reentry problem has raised the question of the thermal stability of propellant fuels during the reentry portion of the flight path when the temperature of the fuel tanks will be raised due to high aerodynamic heating rates. Both the residual fuel and its vapors will be exposed to the high wall temperatures of the tank. If the wall temperature were higher than the self-ignition temperature of the fuel vapor of liquid, ignition would occur with accompanying rapid increase in both temperature and pressure. A part of this hazard can be eliminated by flushing the fuel tank with an inert gas, such as helium or nitrogen; however, the question still remains whether or not the fuel would decompose spontaneously.

Such propellant combinations as UDMH—nitrogen tetroxide, and hydrazine —nitrogen tetroxide have been proposed for rocket systems. On decomposing, these fuels release large quantities of gas, and even in a vented system could produce considerable pressure buildup. It has been suggested that mixing diethylenetriamine with UDMH will significantly raise the temperature of decomposition.

The thermal stability of UDMH was investigated in a static system simulating conditions in an almost-empty fuel tank. The self-ignition temperature and spontaneous decomposition temperature of the pure fuel were determined at atmospheric pressure to be 454° and 740° F, respectively, with the larger (740° F) value, obtained in an inert atmosphere of nitrogen, representing the minimum temperature that would cause a rapid exothermic reaction. The addition of 40 weight percent diethylenetriamine to UDMH did not significantly affect these properties.

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WEYMOUTH, F. R., "Hydrazine-Chlorine Trifluoride Combustion and Performance Calculations," Rep. No. 56–982–008, Bell Aircraft Corp., Contract W33–038ac–14169 (Project Rascal), 1947.

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Fire Extinguishment

If the fire hazard is to be minimized, maximum effectiveness in fire extinguishment must be achieved. Research and development in this field have been sponsored and conducted by the Federal Aviation Agency, the Air Force, the Navy's Bureau of Aeronautics, and other government and private laboratories. Although these investigations have been extensive, the majority have been predominantly of the applied rather than fundamental nature. Emphasis has been placed on such factors as methods of application of extinguishing agents, optimum rates of application, and minimum effective quantities required.

NATURE OF EXTINGUISHMENT ACTIONS

The actions by which extinguishing agents put out fires may be classified as (1) physical actions, and (2) chemical actions. The physical actions include:

1. Cooling action which lowers the temperature of the combustible substance below its ignition temperature.
2. Blanketing action which prevents air from reaching the fire and results in a dilution of the oxygen content of the surroundings.
3. Mechanical action which results from directing the agent across the fire with sufficient force to cut the flame away from the combustible.

The chemical actions include (1) chain-breaking and (2) "preferential-oxidation."

The chemical actions are complex. A complete understanding of them ultimately depends upon a complete understanding of the combustion mechanisms. In the case of the hydrocarbon compounds the combustion processes are so intricate and complex that a rational scientific solution of them is impossible at present. It has been fairly well established that hydrocarbon combustions, like the hydrogen and carbon-monoxide combustions, proceed by branched-chain

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mechanisms, although it is not known with certainty what radicals function as the chain carriers. The inhibiting action that minute quantities of the halogens and other substances have on these reactions has been interpreted as one of combination with or deactivation of the chain carriers. This results in a breaking of the reaction chains and a subsequent partial or complete retardation of the reaction. The chain-breaking action is the more important of the two chemical actions of fire-extinguishing agents. The other chemical action, preferential oxidation, which is exhibited by some of the slightly inflammable extinguishing agents, is the reaction of the agent with the ambient oxygen and results in a smothering of the fire.

RELATIVE IMPORTANCE OF THE DIFFERENT ACTIONS

Some, and possibly all, of the five actions of fire-extinguishing agents are operative during the extinguishing of a fire. Evaluation of their relative importance becomes very complex. The gaseous and liquid extinguishing agents will be considered first, then the metallic salts.

The mechanical action is primarily a function of the method of application. Since it is dependent on the manner in which the agent strikes across the flame, it is probably of major importance in extinguishing most aircraft fires. The blanketing action is mainly a function of the rate of application but also depends on the volatility and the density of the extinguishing agent. The FAA found that the rate of application is the most important factor affecting the ability of an agent to extinguish fires. From this fact, it would seem that the blanketing action of extinguishing agents is one of the most important actions.

Cooling action is a function of the physical properties of the agent (that is, heat capacity, thermal conductivity, and the heat of vaporization) and is of different magnitude for different agents. The differences in extinguishing effectiveness of the various inert gases (helium, argon, nitrogen, carbon dioxide, and water vapor), as measured in inflammable-limits studies, are adequately explained by differences in cooling action. The cooling action obviously is also a function of the amount of extinguishing agent employed. With most extinguishing agents, except water and highly compressed carbon dioxide, the amounts used are small and the cooling action is of only secondary importance.

The importance of the chemical actions are indicated by the greatly enhanced extinguishing effectiveness of the gaseous and liquid halogen-containing compounds, as determined in inflammable-limits studies. These compounds have larger specific heats than the inert gases and

the cooling action should therefore be increased, but the increase is not large enough to account for the much greater effectiveness of many of the compounds investigated. Among the halogen compounds there is no relation between extinguishing effectiveness and specific heat. This effect therefore must be derived from strong chemical actions.

Although the chemical actions appear much more important than the cooling action, it is difficult to appraise their importance relative to the blanketing and mechanical actions. Such an appraisal could be made from a quantitative correlation between results obtained from inflammable-limits studies, which measure chemical actions (and cooling action), and those obtained by direct-application methods.

For metal salts, the main action appears to be chemical in nature. This is self-evident for water solutions because the addition of the salt can hardly produce any marked change in the cooling and blanketing properties of the water. For dusts and powders, there is little blanketing action; it has been shown that the extinguishing effect arises primarily from the undecomposed salt.

Although the chemical actions appear to be important in fire extinguishing, their importance must not be overemphasized. At present, it is impossible to give a quantitative evaluation of the significance of the chemical actions relative to the blanketing and mechanical actions because no reproducible quantitative data on the relative efficiencies of different agents have been obtained by direct-application methods.

No consideration has been taken of the toxicity of the possible fire-extinguishing substances. Little is known about the toxicity of most of the organic halogen compounds, but it is known that the majority of them will give off toxic vapors when applied to fires. Fortunately, considerable amounts of pungent acid are formed, and these acids give sufficient warning.